PHYSICS AND TECHNIQUES OF ELECTRON TUBES

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VOLUME 1

PRINCIPLES OF VACUUM TECHNIQUE

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FOREWORD

by Prof. G. A. Boutry

In spite of its recent origin, the electronics and radio industrial group is now one of the most powerful in the world.

It has developed broadcasting and telecommunications as new means for the dissemination of ideas and information. It has frequently brought to most human industrial activities simpler and better solutions of the numerous problems of measurement, regulation and control which they often meet. The applications of nuclear physics, which we see budding forth, could not be developed without its assistance.

At the heart of this group there is a section, only small if considered in terms of the number of people employed, which has for a long time indisputably been the sole source for the development and progress of the whole group. This is the electron tube manufacturing industry.

In spite of the more recently developed circuit elements called transistors, this industry will continue to enjoy this leading part in the future. When transistors were first introduced, we thought that they would take the place of electron vacuum tubes. We now know that they are complementary to them and allow new developments. In any case they will never get into severe competition with them, except in a few instances where tubes are not giving complete satisfaction. This is a particular example of one of the greatest laws of industrial development.

Staff training sets difficult problems, which have not yet been completely solved anywhere. Compared with the numbers employed in the chemical and mechanical industries, the staff is limited yet of high technical skill. Primary teaching for these particular industrial techniques is always evolving. In France, as in other countries, specialized schools have been established.

Dr. Champeix, whose teaching style and didactic talent are already well known to numerous students, has taught in several of them

and continues to do so. He initiated a course of studies in Physics and Techniques of Electron Tubes at the École Nationale de Radiotechnique, and is at present lecturing on this at the École Française de Radioélectricité. The matter of these lectures is presented here.

This work unites the best qualities which characterize French technical education — logic, perspicuity and simplicity. Beginners should not be afraid of using it. Whenever necessary the basic laws of physics, on which developments are founded, are re-stated and briefly but sufficiently explained; and it will be found that the mathematical methods used in this book are always quite easy to understand. This does not mean that the author conceals the difficulties or complexities of some of the points he writes about. Whenever he has to simplify either statements of phenomena or arguments, he assists the reader by giving references which will allow them to complete their knowledge later.

The whole book is very pleasant to read. This quality should help to make students like it. Wishing the greatest success to this first volume, I look forward to seeing Dr. Champeix publish very soon the second one, dealing with Electron Tube Theory and Manufacture.

PREFACE

THIS volume is the first part of a course on electron-tube engineering, taught since 1949 at the École Nationale de Radiotechnique and the École Française de Radioélectricité, in Paris.

After this first volume devoted to the basis of vacuum technique, the second one will deal with electron-tube design and technology.

Construction of electron devices using low pressures (receiving and transmitting radio-tubes, cathode-ray tubes, photoelectric cells and derived appliances, gas-filled tubes, X-ray tubes, particle accelerators, etc.), as well as the corresponding researches, employ at present all over the world about 800,000 persons, say 80,000 engineers or scientists, 200,000 technical assistants, and more than 500,000 workers.

Training of technical staff in this profession has always set difficult problems. As a matter of fact, recently graduated engineers seldom know, in vacuum technique, anything other than the rudiments of the kinetic theory of gases.

Consequently, the result is that several years must normally be spent, training the specialists whom tube factories and laboratories need more and more keenly, in this hard but fascinating discipline.

Therefore, I have hoped to do a service to the technical assistants desirous of adding to their acquirements, to the students attracted by the apparently mysterious look of this technique, and to the young engineers starting in this difficult craft, by placing at their disposal a summary of the various fields of knowledge, in theory as well as in practice, which will be required for their work.

My end will be completely achieved if at times a colleague of mine, greatly experienced in vacuum technique, consents to open this book to look for some forgotten information.

I wish to thank warmly the President of the Laboratoires d'Électroniques et de Physique Appliquée, who has kindly authorized the publication of this work.

Finally, my indebtedness to Mr. J. A. Jenkins, who has kindly undertaken the checking of the English translation, is gratefully acknowledged.

R. C.

CHAPTER I

REVIEW OF SOME PRINCIPLES IN PHYSICS

IN THIS chapter, we shall review some general principles necessary for the understanding of the course, but which will not be studied thoroughly later on in the book: these include unit systems, expansion phenomena, heat transmission, pyrometry.

1.1. UNITS

A physical quantity is usually expressed with units. In the CGS system, the *fundamental units* are:

for the length L, the centimetre (cm);

for the mass M, the gramme (g);

for the time T, the second (sec);

for the temperature, the centigrade degree (°C).

The MKSA (Giorgi) system is becoming more and more used. In this system, the fundamental units are the metre (m), the kilogramme (kg), the second (sec) and the ampere (A), the other electric units being those of the old system (the so-called "practical system": volt, ohm, watt, joule, etc.). Table 1.1 gives the equivalences between CGS and MKSA systems.

The derived units are expressed from the fundamental ones.

We call the *dimension equation* of a derived unit, a formula in which there appears the L, M and T symbols, bearing a determinate exponent, positive, negative or null, which shows how the derived unit is connected with the fundamental ones. For instance: a speed is a length divided by a time. This is written as LT^{-1}. If there is any doubt about the validity of an equation in physics, one may calculate the two dimen-

sional equations of its two terms: they must be identical. However, this process does not provide information about the numerical factors.

TABLE 1.1

Size	CGS electromagnetic system		MKSA Giorgi system	
	Dimension	Unit	Value	Unit
Length	L	cm	10^2 cm	m
Mass	M	g	10^3 g	kg
Time	T	sec	1 sec	sec
Surface	L^2	cm^2	10^4 cm^2	m^2
Volume	L^3	cm^3	10^6 cm^3	m^3
Speed	LT^{-1}	cm sec^{-1}	10^2 cm sec^{-1}	m sec^{-1}
Acceleration	LT^{-2}	cm sec^{-2}	10^2 cm sec^{-2}	m sec^{-2}
Force	LMT^{-2}	dyne	10 dynes	newton (N)
Work, energy	L^2MT^{-2}	erg	10 ergs	joule (J)
Power	L^2MT^{-3}	erg sec^{-1}	10 ergs sec^{-1}	watt (W)
Pressure	$L^{-1}MT^{-2}$	barye	10 baryes	N m^{-2} (or pascal)
Potential difference	$L^{3/2}M^{1/2}T^{-2}$		10 CGS	volt (V)
Current intensity	$L^{1/2}M^{1/2}T^{-1}$		1/10 CGS	ampere (A)
Electricity charge	$L^{1/2}M^{1/2}$		1/10 CGS	coulomb (C)
Resistance	LT^{-1}		10 CGS	ohm (Ω)

1.2. REVIEW OF SOME DEFINITIONS

SPEED: 1 m sec^{-1}: speed of a body moving with a uniform movement which covers 1 m per sec.

ACCELERATION: 1 m sec^{-2}: acceleration of a body moving in uniformly accelerated movement, the speed of which is increasing by one metre per second, every second.

FORCE: is defined by the fundamental equation of dynamics:

$$F = m\gamma \tag{1.1}$$

(m = mass; γ = acceleration).

1 newton: a force which supplies an acceleration of 1 m sec^{-2} to a mass of 1 kg.

1 dyne: a force which supplies an acceleration of 1 cm sec^{-2} to a mass of 1 g.

1 gramme-weight: a force which, applied to a 1 g mass, supplies it with an acceleration equal to the weight one, i.e. 981 cm sec^{-2}; then, 1 gramme-weight = 981 dynes.

WORK (or ENERGY): measured by the product of a force F acting against a resistance and the distance l moved against the resistance:

$$W = F\,l. \tag{1.2}$$

1 joule: work done by a force of 1 newton acting through a distance of 1 m.

1 erg: work done by a force of 1 dyne acting through a distance of 1 cm. Then, 1 erg = 10^{-7} joule.

1 kg = 9·81 joules.

1 kWh = 3600×10^3 joules.

POWER: the time rate at which work is done $P = W/t$ (W = work; t = time).

1 watt = 1 joule sec^{-1} = 10^{-7} erg sec^{-1}.

1 kg sec^{-1} = 9·81 joules sec^{-1}.

1 CV = 75 kg sec^{-1} = 736 watts.

1 HP = 746 watts.

PRESSURE: ratio of the force to the surface on which force is applied:

$p = F/S$ (F = force; S = surface).

1 pascal: 1 N m^{-2}.

1 barye = 1 dyne cm^{-2} = $0{\cdot}75 \times 10^{-3}$ mm Hg = 0·1 pascal.

1 mm Hg† = 1333 baryes.

1 normal atmosphere = 760 mm Hg = 1013×10^3 baryes $\simeq$ 1 bar.

Let us calculate the equivalence between 1 barye and 1 mm Hg.

We have to find out the pressure necessary to balance the normal height of the mercury column in a barometer, i.e. 760 mm (Fig. 1.1).

According to Pascal's equation, we have:

$$p_B - p_A = h\,\varrho\,g \tag{1.3}$$

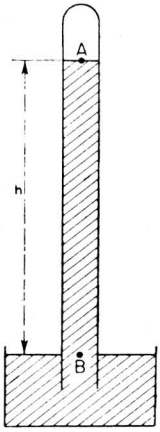


FIG. 1.1

† Abbreviation for "millimetre of mercury". In Germany this is called a Torr.

(ϱ = mercury density; g = gravity acceleration= 981 cm sec^{-2}). p_A being nearly zero, we may write:

$$760\,\text{mm Hg} = p_B = h\varrho g = 76 \times 13{\cdot}6 \times 981 \text{ dynes cm}^{-2}$$
$$= 1013 \times 10^3 \text{ baryes.}$$

It is preferable to use the barye; it is one of the only rational units. Physicists, however, are very fond of the millimetre of mercury, owing to its direct physical meaning.

Flows of gases. These are expressed, as required, in varied coherent units: litres per second (l./sec), cubic centimetres per second (cm^3/sec), cubic metres per hour (m^3/hr) . . . etc. Of course, it is essential to define the pressure at which volumes are measured.

Very small flows of gases, such as those given by "leaks", are often expressed in *lusec*. 1 lusec is a flow of gas of 1 litre per second, measured at a pressure of 10^{-3} mm Hg (1 μ).

1.3. THERMODYNAMICS

1.3.1. Temperature

The temperature idea is an intuitive one. We easily feel the difference between a hot and a cold body. On the other hand, we know that if we heat a body, we change its physical characteristics (dimensions, density, electric and optical properties).

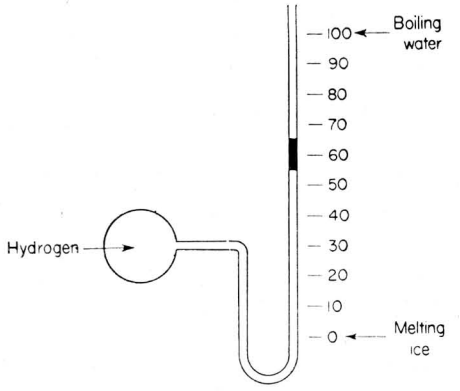


FIG. 1.2

The *standard scale* is obtained by dipping, in succession, first in melting ice, then in boiling water, a gas-thermometer provided with a mercury index: thus, the pressure variation of the gas at constant volume is used as a thermometric phenomenon. The interval is divided into a hundred equal parts, every one of which constitutes a *centigrade degree* (°C) (Fig. 1.2).

As gas pressure decreases by 1/273 of its value at 0°C every time the temperature decreases by 1°, we can understand it is impossible to go down below −273°C. This is what we call the *absolute zero.*

Consequently, the absolute scale is obtained by adding 273 degrees to the Centigrade temperature; now it is stated in Kelvin degrees (°K).

1.3.2. **Thermal expansion**

A metallic rod gets longer when it is heated. To a first approximation, we shall admit that this expansion is reversible. Between 0° and 100°C, the curve:

$$\Delta l = l_\theta - l_0 = f(\theta)$$

is almost a straight line (Fig. 1.3). Hence:

$$l_\theta - l_0 = l_0 \alpha \theta$$

and:

$$l_\theta = l_0 (1 + \alpha \theta) \qquad (1.4)$$

where α is the *average linear expansion coefficient* of the metal between 0 and θ.

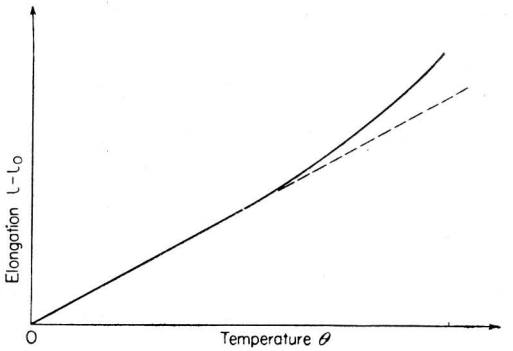


FIG. 1.3

For high temperatures, the curve is usually not a straight line. It is then represented by a function, such as:

$$l_\theta = l_0 (1 + \alpha \theta + \beta \theta^2 + \\ + \gamma \theta^3 + \cdots). \qquad (1.5)$$

Application to radio tubes

Expansion phenomena are very important for tube engineering.

(a) The electrodes apt to expand by a heating effect must be able to do so without any bending. This is the reason why grids, cathodes, etc., must slip smoothly inside the spacers holding them (Fig. 1.4).

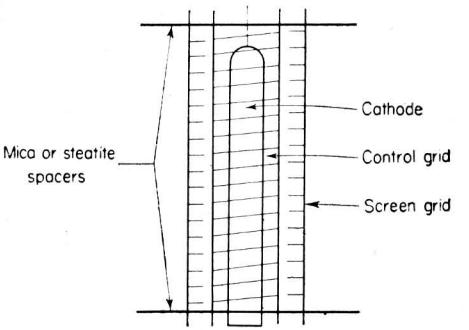


FIG. 1.4

(b) The conducting wires which connect electrically the tube electrodes to the external circuit must have the same expansion coeffi-

TABLE 1.2

LINEAR EXPANSION COEFFICIENTS OF SOME MATERIALS $(°C)^{-1}$

Nickel	13×10^{-6}	Quartz	$0{\cdot}6 \times 10^{-6}$
Copper	16×10^{-6}	Pyrex	$3{\cdot}5 \times 10^{-6}$
Iron	12×10^{-6}	Lead-glass	$8{\cdot}5 \times 10^{-6}$
Platinum	9×10^{-6}	Lime-glass	$9{\cdot}5 \times 10^{-6}$
Tungsten	$4{\cdot}5 \times 10^{-6}$		
Molybdenum	$5{\cdot}5 \times 10^{-6}$		
Copperclad†	9×10^{-6}		

cient as the glass they pass through, in order not to produce any air-leak.

(c) There should only be sealed together glasses with an equal or nearly equal expansion coefficient in order to avoid cracks. If very different glasses have to be joined, graded seals can be built up (Fig. 1.5).

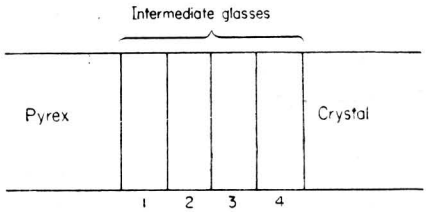


FIG. 1.5

1.3.3. **Specific heat**

What we call the *specific heat* of a substance is the quantity of heat to be supplied to 1 g of this substance to increase its temperature by 1°C. It is computed in cal g^{-1} $(°C)^{-1}$. Water is the substance which has the highest specific heat (in addition it is used to define the calorie): 1 cal g^{-1} $(°C)^{-1}$.

1.3.4. **Heat transfer**

Heat may be transmitted by three means: by conduction, by convection, by radiation.

1.3.4.1. *Thermal Conduction*

This is the transfer of heat from the hot part to the cold one of a single body, or through two bodies in contact.

Let us consider a plate of a thickness x, one of the walls being at the temperature θ_1, and the other one at the temperature θ_2 (Fig. 1.6).

† Copper-coated nickel-iron alloy, capable of being sealed to lead-glass and to lime-glass (see Vol. II, Chap. XII).

TABLE 1.3
Thermal Conductivity Coefficient and Electric Resistivity of some Materials

Good conducting materials			Weak conducting materials			Bad conducting materials	
Material	λ (CGS)	ϱ (electric resisti-vity) $10^{-6}\Omega$ cm	Material	λ (CGS)	ϱ (electric resisti-vity) $10^{-6}\Omega$ cm	Material	λ (CGS)
Silver	1·01	1·6	Zinc	0·3	6	Marble	0·007
Copper	0·92	1·7	Iron	0·16	10	Porcelain	0·003
Gold	0·70	2·4	Tin	0·15	11·5	Glass	0·002
Aluminium	0·48	2·8	Lead	0·08	22	Silica	0·002
Tungsten	0·4	5·5	Constantan	0·06	49	Rubber	0·0005

The quantity of heat passing from one wall to the other one, per second, is:

$$Q = \frac{\lambda S (\theta_1 - \theta_2)}{x} \text{ cal sec}^{-1}, \qquad (1.6)$$

where λ is the *thermal conductivity coefficient* of the considered material (cal cm^{-1} sec^{-1} $(°\text{C})^{-1}$ in CGS units) and S is the plate surface area.

For metals, one may notice the parallelism between thermal and electric conductivity: this is *Wiedemann–Franz's law*. Sometimes it may be useful to compare thermal conductances of two metals by checking their resistivities.

If we have to deal with a rod of an undefined length, heated at one end to a temperature θ_0 (Fig. 1.7), the temperature at a distance x may be calculated by:

$$\theta_1 = \theta_0 \exp\left[-x\sqrt{\left(\frac{\varepsilon P}{\lambda S}\right)}\right] \qquad (1.7)$$

where:

P = perimeter; S = section; x = distance;
ε = exchange factor (between the metal and the room-air);
λ = thermal conductivity coefficient.

This formula is difficult to use. We may use it to compare two wires with the same diameter and the same surface state. We raise

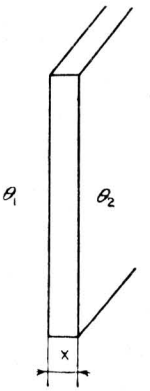


FIG. 1.6

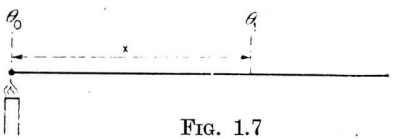


FIG. 1.7

one of their ends to the same temperature θ_0 and we measure the distances x_1 and x_2, for which temperatures θ_1 are the same:

We obtain then:

$$\frac{\lambda_1}{\lambda_2} = \left[\frac{x_1}{x_2}\right]^2. \tag{1.8}$$

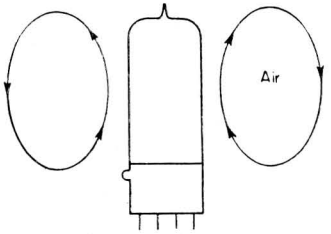
Application to radio-tubes

Control grids must be well cooled to keep down the grid emission (see Vol. II, Sec. 13.5.2). It is then necessary to construct with a good conducting material (pure copper or silver–copper alloy) the grid-rods on which the winding wires are clamped.

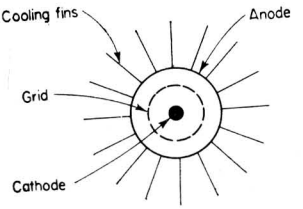
Inversely, mica or ceramic spacers fixing the electrode gaps must be designed so as to cool down the cathode as little as possible.

1.3.4.2. *Heat Convection*

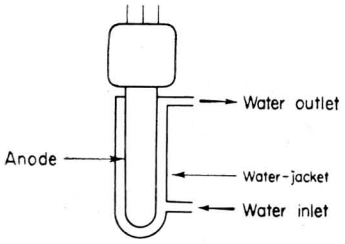
This is the transfer of heat by circulation of a fluid (a gas or a liquid) around the heated body. It may be *natural* or *forced.* Inside a vacuum tube, and, in general, when the pressure falls below one barye, it may



(a) small receiving tube cooled by natural convection



(b) Small transmitting tube cooled by forced convection



(c) Large transmitting tube cooled by water circulation

FIG. 1.8

be neglected. It is not the same for gas-filled tubes: for instance, in gas-filled triodes (thyratrons) the cooling of the cathode by convection is important enough to have to increase significantly the heating power. We shall see that, in some special tubes (iron–hydrogen regulators tubes), convection plays a main part (Vol. II, Sec. 11.7).

Application to radio tubes

In small radio tubes, it is partly convection which cools down the bulb walls. Consequently, it is necessary to provide sufficient ventilation for apparatus (cases and covers are perforated, etc.).

In big transmitting tubes, natural convection is insufficient to remove all the heat supplied to the anode; this is the reason why water-circulation is very often used. However, when we want to avoid this, we may provide the anode (which is also used as the bulb) with fins which are cooled down with an air-blower (Fig. 1.8) (see also Vol. II, Sec 13.6).

1.3.4.3. *Thermal Radiation*

Every body when heated radiates energy all over the electromagnetic spectrum.

DEFINITIONS. Let us consider a body on which there falls a light ray coming from a monochromatic light source S, with a wavelength λ (Fig. 1.9).

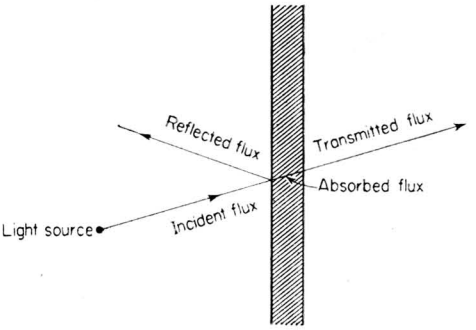


FIG. 1.9

We call:

Transmission coefficient τ_λ, the ratio of the transmitted flux to the incident flux.

Reflection coefficient ϱ_λ, the ratio of the reflected flux to the incident flux.

Absorption coefficient α_λ, the ratio of the absorbed flux to the incident flux.

Obviously, it follows that:

$$\tau_\lambda + \varrho_\lambda + \alpha_\lambda = 1. \tag{1.9}$$

If it is an *opaque* body, we have $\tau_\lambda = 0$, whence $\varrho_\lambda + \alpha_\lambda = 1$. We call *black body*, an opaque body whose reflection coefficient would be zero for every wavelength, i.e. $\alpha_\lambda = 1$. A non-black body is a body with $\alpha_\lambda < 1$.

No known surface has $\alpha_\lambda = 1$. Lamp-black gets very near to it with $\alpha_\lambda \simeq 0{\cdot}98$. It is possible to approach still nearer by drilling a little hole in an homogeneous temperature cavity. A light ray which goes through the hole carries out a certain number of reflections quickly absorbing it (Fig. 1.10).

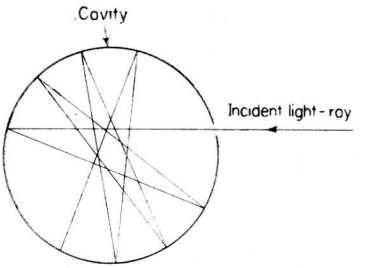


FIG. 1.10

We call *spectral emission coefficient* or *spectral emissivity* ε_λ of a

body, the ratio of the power radiated by this body, to the power radiated by the same surface of a black body raised to the same temperature, in both cases for a given wavelength λ.

Kirchoff's law. The emission coefficient of a body is equal to its absorption coefficient:

$$\varepsilon_\lambda = \alpha_\lambda. \tag{1.10}$$

Therefore, for a black body:

$$\varrho_\lambda + \varepsilon_\lambda = 1. \tag{1.11}$$

This relation enables us to deduce ε_λ by measuring ϱ_λ.

Planck's formula. This allows us to study the radiation of a heated body.

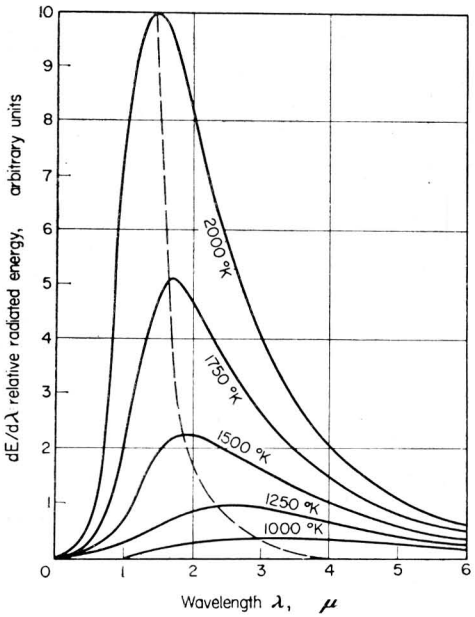


FIG. 1.11

The energy radiated per sec and per cm² in terms of temperature and wavelength, is given by:

$$\frac{\mathrm{d}E_\lambda}{\mathrm{d}\lambda} = c_1 \lambda^{-5} \frac{1}{\mathrm{e}^{c_2/\lambda T} - 1} \tag{1.12}$$

with:

$$c_1 = 3{\cdot}7 \times 10^{-5} \text{ erg sec}^{-1} \text{ cm}^{-2}$$

and

$$c_2 = 1{\cdot}432 \text{ cm } °\text{K}.$$

Drawing the curves $\mathrm{d}E_\lambda/\mathrm{d}\lambda = f(\lambda)$ (Fig. 1.11) with temperature as parameter, we may notice the following points:

(a) At any temperature, the radiation of a heated body occurs *all over* the electromagnetic spectrum.† In particular, there is always radiation at wavelengths, no matter how long. (With a radio receiver, in the centimetric waveband, it is possible to detect the hertzian radiation of a heated metal ingot.)

† The different regions of the electromagnetic spectrum are represented in Vol. II, Fig. 3.10.

(b) For each temperature, however, there is a preferential wavelength around which the greatest part of the energy is radiated. It is easy to see that this wavelength λ_m moves to lower and lower values when the temperature is rising, according to the equation:

$$\lambda_m T = \frac{c_2}{4{\cdot}965} = \text{constant}. \tag{1.13}$$

This is the *Wien law.*

Particularly, in order that this preferential wavelength takes place in the middle of the visible spectrum (0·4 to 0·7 μ, mean value: 0·55 μ), it would be necessary to reach a temperature around 6000°K; this is the case of the sun.

Stefan–Boltzmann formula. We obtain the total power radiated per cm² of a black body by calculating:

$$P = \int_0^\infty \frac{\mathrm{d}E_\lambda}{\mathrm{d}\lambda}\,\mathrm{d}\lambda \tag{1.14}$$

that gives:

$$P = \sigma\,(T^4 - T_0^4) \tag{1.15}$$

with σ = Stefan–Boltzmann constant = $5{\cdot}7 \times 10^{-12}$ W cm^{-2} (°K)$^{-4}$. T_0 is the room temperature, which we may neglect very often when $T > T_0$.

If the body is not a black body, it is necessary to multiply the above expression by a factor ε_t, named *total emission coefficient*, or *total emissivity* of the body.

Taking into account the surface S, we have:

$$\boxed{P = S\,\varepsilon_t\,\sigma\,(T^4 - T_0^4)}\,. \tag{1.16}$$

We call *grey body*, a non-black body whose curves are deduced from the black-body ones by simple homothety.

In this case

$$\varepsilon_t = \varepsilon_\lambda.$$

Usually ε_λ varies from one wavelength to another and is consequently different from ε_t (see Table 1.4).

Application to radio tubes

In electron vacuum tubes, electrodes lose their heat only by conduction or radiation. This last phenomenon usually prevails. If it is

required to cool down an anode more efficiently, it must be blackened, which increases ε_t, and it is provided with fins, so increasing S. But it is necessary not to put on too many fins, because one single fin surrounded with others at the same temperature would not radiate at all (T_0 ranging about T).

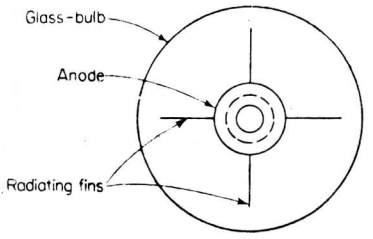


FIG. 1.12

Furthermore, the control grids of certain tubes very often have blackened fins at their ends, in order to reduce the grid temperatures and to avoid thermionic emission (see Vol. II, Chap. XIII and XIV).

EXERCISE. A 6V6 power pentode, working under static conditions, operates with a plate current of 36 mA, and a plate voltage of 250 V. The anode surface is 15 cm^2, and the total emissivity is 0·8. Conduction losses are supposed to be of 0·5 W, and room temperature 27°C. Calculate the anode temperature.

Solution. The temperature will be deduced from formula (1.16). But we only have to consider the power dissipated by radiation, then:

$$9 - 0{\cdot}5 = 15 \times 0{\cdot}8 \times 5{\cdot}7 \times 10^{-12} (T^4 - 300^4).$$

We obtain:

$$T = 603°\text{K} = 330°\text{C}.$$

It will be observed we did not take into account the thermal energy produced by the cathode whose radiation will, of course, contribute to raise the anode temperature.

1.3.5. **Temperature measurement**

Classical thermometers use the expansion of solids, liquids or gases. We shall not dwell on this point.

We shall, however, review some electrical or optical methods used for electron tube design or manufacture.

1.3.5.1. *Electrical Methods*

The resistance method. The resistivity of a metal increases with temperature. The resistance formula is the same as the expansion one:

$$R = R_0 (1 + \alpha \theta + \beta \theta^2 + \cdots). \qquad (1.17)$$

Knowing the constants α and β, or better, the curve $R = f(\theta)$, one may roughly estimate the temperature of a filament, a heater, etc.

A similar phenomenon is used in certain vacuum gauges (Pirani) (see Sec. 6.4.1).

The thermocouple method. When two different metals are welded together and connected to a galvanometer, and when the welded point is heated, a current is obtained depending on the difference of the temperature between the hot welded point and the other parts of the circuit.

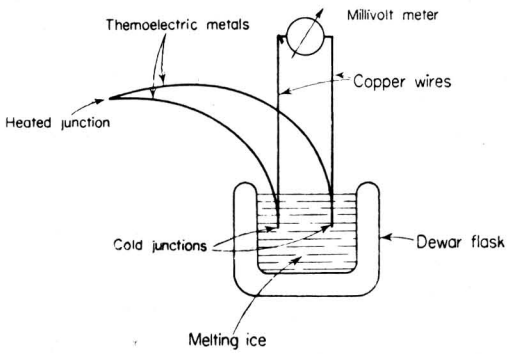


FIG. 1.13

It is necessary to define accurately the temperature of the cold junction (Fig. 1.13).

For certain metals, thermoelectric e.m.f. is nearly proportional to the difference temperature $\Delta\theta$ between the two welded points.

Examples of common couples:

couple { pure platinum / platinum + 10% rhodium } e.m.f. about 1 mV for $\Delta\theta = 100°C$,

couple { Chromel (10% Cr + 90% Ni) / Alumel (4% Al + 96% Ni) } e.m.f. about 5 mV for $\Delta\theta = 100°C$.

To obtain good accuracy, it is better to measure e.m.f. with a potentiometric system, using the opposition method.

Thermoelectric phenomena have great theoretical importance: they provide one of the few ways (with the thermionic effect) of converting directly thermal energy into electric energy. They are obviously subject to Carnot's principle.

1.3.5.2. *Optical Methods*

The total radiation pyrometer. A concave mirror receives radiation issuing from the source to be pyrometered and throws it back to the

thermocouple. It is not necessary for the radiation to be visible. This method is liable to many sources of error: defect of focusing, absorption by the intermediate medium, etc.

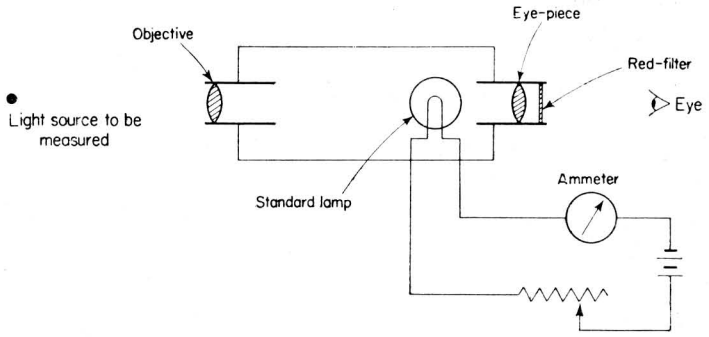


FIG. 1.14

The disappearing filament pyrometer. This is a small telescope allowing one to see the source, superimposed on the image of a tungsten filament standard lamp (Fig. 1.14). This filament is heated by a battery,

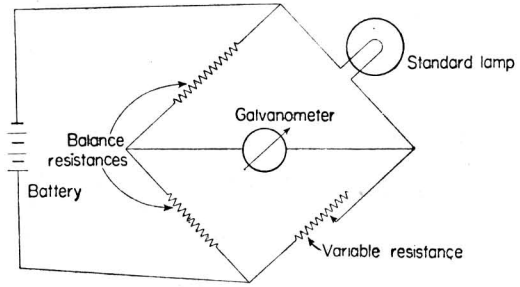


FIG. 1.15

a rheostat and an ammeter. The filament is heated so that its image has the same brightness as that of the source; then it cannot be discerned: it "disappears". The ammeter is then calibrated from a black body, the temperature of which is measured with a thermocouple. If the source total emissivity is not equal to 1, it must be taken into account. The wavelength is defined by a filter put on the viewing side (usually $\lambda = 0{\cdot}65\,\mu$). The apparent temperature obtained is called

the *brightness temperature* T'. Planck's formula (eq. 1.16) enables us to calculate the correction giving the true temperature T:

$$T = \frac{T'}{1 + T' \dfrac{\lambda}{c_2} \operatorname{Log} \varepsilon_\lambda}$$

where λ is the wavelength of the filter, ε_λ is the spectral emissivity and c_2 is the second radiation constant of eq. 1.12.

To increase the sensitivity, a bridge-circuit is usually built up (Fig. 1.15).

In an alternative (Ribaud's pyrometer), the filament current is kept constant and regulated to the required maximum; an absorbing filter made of neutral glass with a regularly varying thickness slides in front of the front lens, reducing as required the source brightness. The filter shift is bound up with the temperature scale.

TABLE 1.4

TOTAL EMISSION AND SPECTRAL EMISSION COEFFICIENTS

Bodies	ε_t							ε_λ for $\lambda = 0{\cdot}65\mu$
	20°C	100°C	500°C	1000°C	1500°C	2000°C	2500°C	
Aluminium n. ox.	0·022	0·028	0·06					
ox.		0·1	0·18					
Alumina								0·2–0·4
Chromium n. ox.		0·08						0·34
Copper n. ox.		0·02			0·15			0·10
Iron n. ox.		0·05		0·08	0·13			0·35
ox.		0·74	0·84	0·88				
Silver n. ox.		0·02	0·35					
Magnesia			0·24	0·18	0·17			0·1–0·4
Molyb-denum n. ox.				0·13	0·19	0·24		0·37
Nickel n. ox.	0·045	0·06	0·12	0·19				0·36
Gold n. ox.		0·02	0·03					0·14
Platinum n. ox.	0·037	0·047	0·096	0·152	0·191			0·3
Tantalum n. ox.					0·21	0·26		0·49
Thoria			0·21	0·22	0·23			0·2–0·57
Tophet A and C			0·9					0·9
Tungsten n. ox.	0·024	0·032	0·07	0·15	0·23	0·28	0·32	0·43
Graphite				0·52	0·52	0·52		0·81–0·9
BaO + SrO†				0·25				0·1–0·3

† Mixture constituting the layer of oxide-coated cathodes (see Vol. II, Chap. IV).

The disappearing filament pyrometer enables one to measure with an accuracy greater than 1°C out of 1000. In addition, it is not very sensitive to the nature of the intermediate medium (little absorption by glass, water vapour, etc.). On the other hand, it needs an operating procedure for each reading.

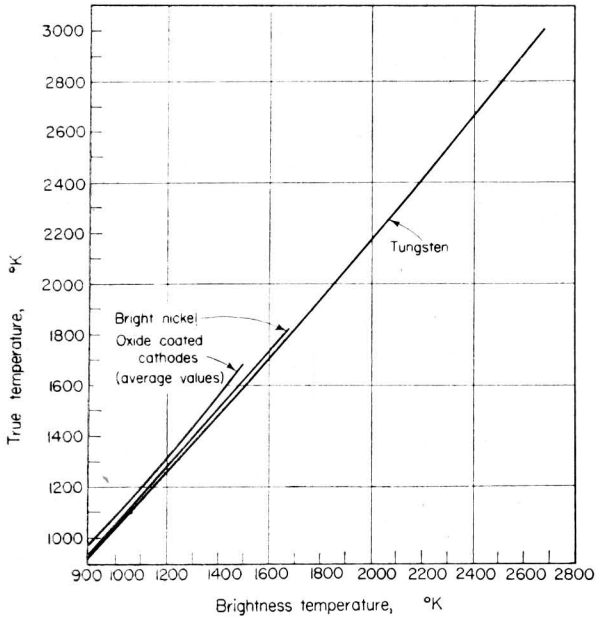


FIG. 1.16

Table 1.4 gives total and spectral emissivity of a certain number of bodies used in electron tube technique.

Figure 1.16 gives, for some surfaces, the true temperature against the brightness temperature; the latter has been measured with a pyrometer using a filter of $\lambda = 0{\cdot}65\,\mu$.

CHAPTER II

THE LAWS OF THE GASEOUS STATE

PLAN OF THIS CHAPTER

1. First we shall review laws known as "*laws of ideal gases*", relating to the macroscopical state of gases considered as continuous fluids. They concern relations between some overall characteristics of gases, such as pressure, volume, temperature, density, etc.

2. Then we shall investigate the *molecular characteristics* of gases, considered as being composed of distinct particles of which we shall study the speed, the direction, the energy, the mass, the diameter, etc.

3. We shall use the acquired notions to study, in the body of a gaseous mass, *the transfer* of characteristics connected with molecular thermal agitation.

4. We shall end this chapter with some elements of *gas dynamics*, that is the study of laws which control the motion of a mass of gas moving with respect to the vessel containing it.

2.1. LAWS OF THE MACROSCOPIC STATE OR LAWS OF IDEAL GASES

MOST gases obey the laws below, at least for average values of the temperature and of the pressure. Conversely they are notably deviated from for high concentration states: low temperature, high pressure.

2.1.1. **Avogadro's law**

The molecular weights M of different gases are proportional to their densities d in relation to air:

$$\boxed{M = 28{\cdot}95\, d} \quad . \tag{2.1}$$

Oxygen is taken as a basis: $O_2 = 32$ ($d = 1{\cdot}1053$).

For every gas, a mass equal in grammes to the molecular weight fills a volume of 22,414 cm. It is the *molecular volume;* it is of course the

volume of 32 g oxygen, of 28 g nitrogen, etc., and this for *standard conditions of temperature and pressure* (0°C, 760 mm Hg).†

2.1.2. **Boyle's law**

This concerns isothermal changes, i.e. those in which temperature remains constant.

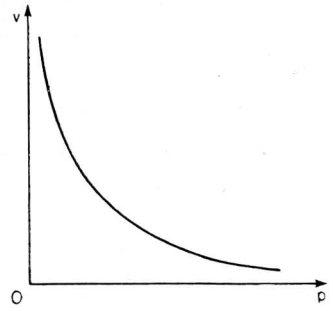


FIG. 2.1

The product of the pressure by the volume remains constant, for a determinate mass of gas:

$$\boxed{p\,v = \text{a constant}} \quad . \tag{2.2}$$

The curve $v = f(p)$ is an hyperbola (Fig. 2.1).

2.1.3. **Gay-Lussac's laws**

They affect changes at constant volume or constant pressure:‡

$$\boxed{\begin{aligned} v &= v_0\,(1 + \alpha\,t) \\ p &= p_0\,(1 + \beta\,t) \end{aligned}} \quad . \tag{2.3, 2.4}$$

p_0 and v_0 being p and v values at 0°C.

It is demonstrated experimentally that:

$$\alpha = \beta = \frac{1}{273}\ °C^{-1}. \tag{2.5}$$

2.1.4. **Formulae for ideal gases**

Avogadro's, Boyle's and Gay-Lussac's laws may be condensed in a single formula:

$$\boxed{p\,v = p_0\,v_0\,(1 + \alpha\,t)} \tag{2.6}$$

In fact, let us consider the same gaseous mass, successively taken under the three states:

(a) p, v, t
(b) p_0, v_0, 0°C
(c) p_1, v_0, t

† Afterwards we shall indicate these conditions by the letters S. T. P.

‡ In all the following, t represents Centigrade temperatures and T absolute temperatures.

this last state being obtained by carrying the gas from (a) to (c) without any change of temperature, that involves:

$$p\,v = p_1\,v_0. \tag{2.7}$$

Now, it may be written between (b) and (c):

$$p_1 = p_0\,(1 + \alpha\,t) \tag{2.8}$$

whence:

$$p\,v = p_0\,v_0\,(1 + \alpha\,t)$$

which is the required result.

Let us write down:

$$1 + \alpha\,t = \alpha\,T \tag{2.9}$$

which gives:

$$T = t + 273. \tag{2.10}$$

This becomes:

$$p\,v = p_0\,v_0\,\alpha\,T. \tag{2.11}$$

Let us take a mass of gas equal to the molecular weight. Its volume V is the molecular volume at standard temperature and pressure conditions. We have then:

$$P\,V = P_0\,V_0\,\alpha\,T. \tag{2.12}$$

Taking:

$$P_0 = 760 \text{ mm Hg} = 1{\cdot}013 \times 10^6 \text{ baryes},$$

$$V_0 = 22{,}414 \text{ cm}^3$$

there is obtained:

$$P_0\,V_0\,\alpha = R = 8{\cdot}31 \times 10^7 \text{ erg } {}^\circ\text{K}^{-1} \tag{2.13}$$

whence:

$$\boxed{P\,V = R\,T}\,. \tag{2.14}$$

R is the *universal gas constant for a gramme-molecule* (or *mole*). It is the energy to be supplied to a gramme-molecule of any gas to increase its temperature by one degree.

2.2. LAWS OF THE MOLECULAR STATE OR KINETIC THEORY OF GASES

2.2.1. **Avogadro's number**

The mass m of the molecules of each gas has been determined experimentally. The *Avogadro number* N is obtained by the ratio of

the mass M of the gramme-molecule to the mass m of one single molecule. *It is the same number for all the gases*:

$$N = \frac{M}{m} = 6{\cdot}02 \times 10^{23} \text{ molecules per mole.} \tag{2.15}$$

It is the number of molecules contained in one gramme-molecule.

There is another constant very often used:

$$k = \frac{R}{N} = 1{\cdot}38 \times 10^{-16} \text{ erg } ^\circ\text{K}^{-1}. \tag{2.16}$$

This is the *Boltzmann constant*, or the *universal gas constant related to one molecule.*†

2.2.2. Basis of kinetic theory of gases

The hypothesis below, which has been used for the working out of gas kinetic theory, has been later widely confirmed by experience.

It will be assumed:

(a) that a gas is formed of distinct molecules, agitated by a continuous random motion.

(b) that molecules have a reciprocal action only when they collide; this allows one to assume that molecular paths are formed by broken straight lines.

(c) that heat is not considered here as a kind of energy different from kinetic energy of moving molecules.

The more a gas is heated, the more the thermal agitation (i. e. the velocities) of molecules rises (whence arises the thermal expansion).

(d) that, because of their continual collisions, molecular velocities are continuously changed. However, as these molecules are numerous, even at low pressures,‡ the laws of Probability Theory may be applied.

One assumes that, at every moment, there is the same number of molecules having a certain direction and a certain velocity. The moment just after, these molecules have changed their velocity and direction, but others have reached them. We say there is a *stationary distribution of velocities*, the so-called *Maxwell-Boltzmann's distribution.*

(e) that the gas is *isotropic*, i.e. there is no preferred direction.

† Consequently note that:

$$\frac{m}{k} = \frac{M}{R}. \tag{2.17}$$

‡ In 1 mm³ of air at 10^{-6} mm Hg, there are still 3×10^7 molecules.

2.2.3. Definition of pressure in the kinetic theory

In these conditions, it is evident that the pressure p of a gas is due to the collision of molecules with the walls of the containing vessel. Let us try to connect this pressure with the other parameters: velocity, number of molecules per cm^3, temperature, etc.

Let us consider a molecule with a mass m striking a wall normally (Fig. 2.2). As the collision is supposed to be perfectly elastic, the change of velocity is $u - (-u) = 2u$.

Therefore the force produced by this collision is:

$$F = m \frac{\Delta u}{\Delta t} = \frac{2 m u}{\Delta t} . \tag{2.18}$$

Thus we have:

$$p = \frac{F}{S} = \frac{2 m u}{S \Delta t} . \tag{2.19}$$

This equation gives the pressure exerted by a molecule reaching the wall at each interval of time Δt.

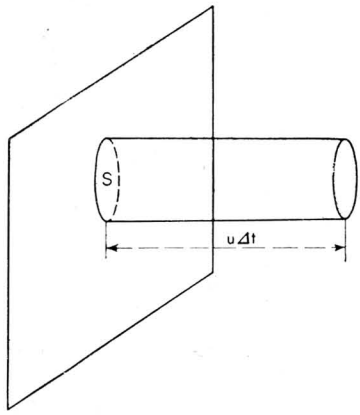


FIG. 2.2

If, during this same interval Δt, n_t molecules are coming too, we have:

$$p = \frac{2 n_t m u}{S \Delta t} . \tag{2.20}$$

Now, we call n *the number of molecules contained in the unit-volume*; let us find the pressure produced by these n molecules.

Consider a cylinder the base of which would be the surface S, and the length of which would be the distance travelled by a molecule during a time-interval Δt, say $u \times \Delta t$. During this time Δt, the base S is struck by:

$$n_t = \frac{n S u \Delta t}{2} \text{ molecules.} \tag{2.20 a}$$

The factor 2 takes into account that only half of the molecules are going to each base. Then we obtain (2.20) as:

$$p = n m u^2. \tag{2.21}$$

Now the product $n \times m$ of the molecular-number per unit-volume, by one molecule-mass, is nothing else than the specific mass of the gas:

$$\varrho = n\,m. \tag{2.21a}$$

Thence:

$$p = \varrho\,u^2. \tag{2.22}$$

So, the pressure is equal to the product of the square of the effective velocity† normal to the wall, by the specific mass ϱ.

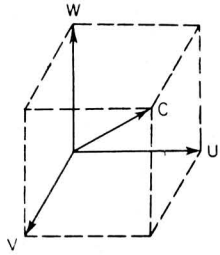


FIG. 2.3

Let us look for a similar relation with the effective velocity in any direction C.

If the three components of the velocity C are named u, v, w, there is obtained (Fig. 2.3):

$$u^2 + v^2 + w^2 = C^2 \tag{2.23}$$

and, for reasons of symmetry:

$$3\,u^2 = C^2 \tag{2.24}$$

thence:

$$p = \frac{1}{3}\,\varrho\,C^2. \tag{2.25}$$

Taking molecular masses and volumes, we may write:

$$\varrho = \frac{M}{V} \tag{2.26}$$

and:

$$p = \frac{1}{3}\,\frac{M}{V}\,C^2 \tag{2.27}$$

whence:

$$p\,V = R\,T = \frac{2}{3}\,\frac{M\,C^2}{2}. \tag{2.28}$$

As a general rule, for a mass of any gas, the product of volume and pressure is equal to two-thirds of the mean kinetic energy of the considered mass of gas.

The above formula allows us to calculate the effective velocity of a gas molecule, depending only on molecular mass and temperature:

$$C = \sqrt{\left(\frac{3\,R\,T}{M}\right)} = \sqrt{\left(\frac{3\,k\,T}{m}\right)}. \tag{2.29}$$

† It will be seen later on that the effective velocity is that corresponding to the mean kinetic energy of the molecules. It is usually known as "root mean square velocity".

Let us calculate the number of molecules n per cm^3 (*molecular concentration*) in terms of pressure:

$$p = n\,m\,u^2 = \frac{n\,m\,C^2}{3} = n\,k\,T \tag{2.30}$$

whence:

$$\boxed{n = \frac{p}{k\,T}} \,. \tag{2.31}$$

It is seen that the molecular concentration does not depend on the nature of the gas.

In standard conditions of temperature and pressure (0°C, 760 mm Hg), the molecular concentration is:

$$n = 2{\cdot}7 \times 10^{19} \text{ molecules per cm}^3.$$

Let the relation between a gas density, pressure and temperature be calculated. It is found that:

$$\boxed{\varrho = n \times m = \frac{p\,m}{k\,T} = \frac{p\,M}{R\,T}} \,. \tag{2.32}$$

Finally, let us calculate the total mass μ of the gas contained in a vessel of volume v in terms of the pressure:

$$\mu = \varrho\,v = p\,v\,\frac{M}{R\,T} \,. \tag{2.33}$$

The Cantor Experiment. A copper leaf, varnished on one side, is placed in a rarefied atmosphere of chlorine (Fig. 2.4).

The leaf is deflected exactly as if a force were exerted on the varnished side. In fact, on this side, chlorine molecules rebound, while on the other side, molecules are absorbed by chemical affinity. The pressure they exert is in the first case twice that of the second one. †

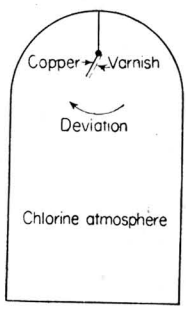


FIG. 2.4

† I have been told by M. L. Dunoyer that a similar experiment is more easily obtained by using a mica leaf on one side of which is stuck powdered phosphoric anhydride, the chlorine atmosphere being replaced by water-vapour.

2.2.4. Maxwell–Boltzmann's distribution function

The manner in which the speeds of the molecules are distributed is represented by a function and a corresponding curve. In order to explain the statistical method employed, an example will be taken from ethnology.

Suppose that we want to plot the curve indicating how the world's population is distributed in terms of age:

From census tables (1954) we shall compute first the number of persons whose age is between 0 and 10 years, then between 10 and 20, etc. (Table 2.1). Then a "stepped" curve (Fig. 2.5) will be plotted

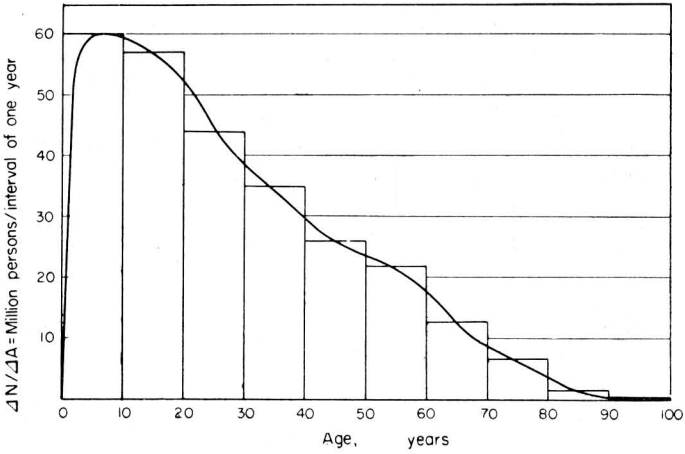


FIG. 2.5

the abscissa of which will be the age A, and the ordinate $\Delta N/\Delta A$, the quotient of the number of persons included in each interval, by the magnitude of this interval.†

In this manner, the surface included between the curve and the axis will represent the total number of the world's population:

$$\sum \frac{\Delta N}{\Delta A} \Delta A = N \tag{2.34}$$

† This process was suggested by J. Millman and S. Seely to illustrate the energy distribution of electrons in metals. (*Electronics*, McGraw-Hill, N. Y., 1941).

and, at the limit, taking intervals of age getting smaller and smaller, a continuous curve will be obtained: $\mathrm{d}N/\mathrm{d}A = f(A)$, with:

$$\int_0^\infty \frac{\mathrm{d}N}{\mathrm{d}A}\,\mathrm{d}A = N. \tag{2.35}$$

Maxwell has worked out a similar function to study the velocity distribution of the gas molecules, that means, to define the number $\mathrm{d}n$

TABLE 2.1

Interval of age	Number (in millions)
0—10 years	600
10—20 years	570
20—30 years	440
30—40 years	350
40—50 years	260
50—60 years	220
60—70 years	128
70—80 years	67
80—90 years	14
90—100 years	1
Total number of world population	2650

of molecules, which, in a given gas, have velocities c included in a small interval between c and $c + \mathrm{d}c$. Therefore it is a function of the following kind:

$$\frac{\mathrm{d}n}{\mathrm{d}c} = f(c).$$

This function, called *the Maxwell–Boltzmann distribution function*, is written as:†

$$\boxed{\frac{\mathrm{d}n}{\mathrm{d}c} = n_1 \sqrt{\left(\frac{2\,m^3}{\pi\,k^3\,T^3}\right)}\,\mathrm{e}^{-\frac{mc^2}{2kT}}\,c^2}\ . \tag{2.36}$$

In this formula, n_1 is the total number of molecules of the considered gas; $\mathrm{d}n$ is the number of molecules with velocities included between

† A simplified demonstration of this formula is given in the Appendix I.

c and $c + \mathrm{d}c$; m is the mass of a molecule; k is the Boltzmann constant; T is the absolute temperature.

Figure 2.6 gives an example of curves corresponding to this function.

Putting $W = m\,c^2/2$, noe obtains the equation of kinetic energy distribution of molecules:

$$\frac{\mathrm{d}n}{\mathrm{d}W} = 2\,n_1 \sqrt{\left(\frac{1}{\pi\,k^3\,T^3}\right)}\,\mathrm{e}^{-\frac{W}{k\,T}}\,W^{1/2}\,. \tag{2.37}$$

Plotting the curve $\mathrm{d}n/\mathrm{d}c = f(c)$, with temperature as a parameter (Fig. 2.6), it is seen that:

1. When increasing velocities are considered, the curve passes through a maximum; this means that at each temperature this maxi-

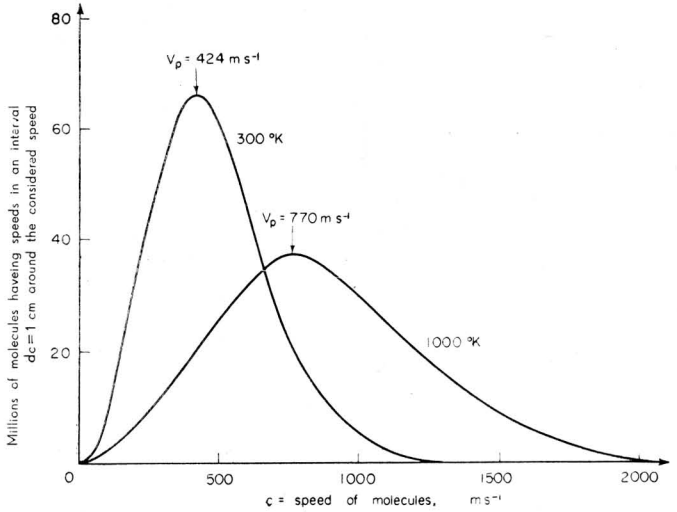


FIG. 2.6

mum corresponds to a velocity known as the "*most probable molecular velocity*".

2. The lower this temperature, the lower the velocities at which this maximum occurs. Particularly, at absolute zero, all the molecules have zero velocity.

3. On the side of high velocities, the curve decreases asymptotically to the abscissa; that means it must always be possible to find

molecules having velocities as high as required. However, these molecules will become fewer and fewer as the velocity becomes higher or the temperature lower.

2.2.5. **Definition of molecular velocities**

2.2.5.1. *The Most Probable Velocity*

This is the one which cancels the derivative of Maxwell–Boltzmann's function. One obtains:

$$\boxed{v_p = \sqrt{\left(\frac{2\,k\,T}{m}\right)}} \,. \tag{2.38}$$

It corresponds with a kinetic energy:

$$W_p = \frac{1}{2}\, m\, v_p^2 = k\, T. \tag{2.39}$$

2.2.5.2. *The Mean Velocity*

This is the velocity obtained by adding up a great number of molecular velocities, then dividing by the number of molecules:

$$\boxed{v_m = \frac{1}{n} \int_0^\infty c\, \mathrm{d}n = \sqrt{\left(\frac{8\,k\,T}{\pi\, m}\right)}} \,. \tag{2.40}$$

2.2.5.3. *The Root Mean Square Velocity*

This is that corresponding to the mean kinetic speed:

$$W_m = \frac{1}{2}\, m\, C^2 = \frac{1}{n} \int_0^\infty \frac{1}{2}\, m\, c^2\, \mathrm{d}n = \frac{3}{2}\, k\, T. \tag{2.41}$$

Whence:

$$\boxed{C = \sqrt{\left(\frac{3\,k\,T}{m}\right)}} \,. \tag{2.42}$$

It is seen that the kinetic energy is connected with the notion of temperature (thermal agitation).

2.2.6. **Mean free path**

This is the mean distance covered by a molecule between two successive collisions (actually a highly varying distance). Let us cal-

culate it. Consider a molecule of diameter d. It will collide with another molecule only if the two centres pass at a distance at most equal to d from one to the other.

Simplifying, it may be supposed that the molecule considered has a diameter equal to $2\,d$, and that the other molecules are mere points. The sphere with a diameter $2\,d$, having the molecule as a centre, is called the *protecting sphere* (Fig. 2.7).

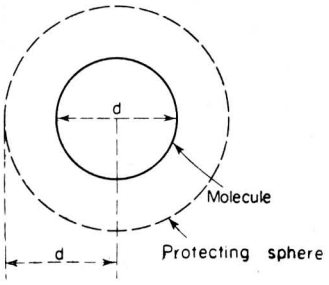


FIG. 2.7

If u is the molecular velocity, the volume swept in 1 sec by the protection sphere is $\pi\,d^2\,u$. If there are n molecules per unit-volume, in the swept volume there will be $\pi\,d^2\,u\,n$ centres of other molecules. This expression is also equal to the number of collisions per sec:

$$\nu = \pi\,d^2\,u\,n. \tag{2.43}$$

Whence the formula of the mean free path (m.f.p.):

$$L = \frac{u}{\nu} = \frac{1}{\pi\,d^2\,n}\,. \tag{2.44}$$

This calculation has been made assuming all the molecules to have similar velocities. In fact, taking into account that these speeds vary according to the Maxwell–Boltzmann distribution law, it would be found out:

$$\boxed{L = \frac{1}{\sqrt{(2)}\,\pi\,d^2\,n} = \frac{k\,T}{\sqrt{(2)}\,\pi\,d^2\,p}}\,. \tag{2.45}$$

TABLE 2.2

MEAN FREE PATH IN AIR AT 20°C

p (mm Hg)	760	100	10	1	10^{-1}	10^{-2}
L (cm)	9×10^{-6}	7×10^{-5}	7×10^{-4}	7×10^{-3}	7×10^{-2}	0·7
p (mm Hg)	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	
L (cm)	7	70	700	7000	70,000	

TABLE 2.3

MOLECULAR CHARACTERISTICS OF SOME GASES OR VAPOURS

Gas	Mass of the molecule (g)	Root mean square speed ($m\ sec^{-1}$)	Diameter of the molecule (cm)
Hydrogen	$3{\cdot}3 \times 10^{-24}$	1910	$2{\cdot}18 \times 10^{-8}$
Helium	$6{\cdot}6 \times 10^{-24}$	1360	$1{\cdot}92 \times 10^{-8}$
Water	$2{\cdot}96 \times 10^{-23}$	640	4×10^{-8}
Nitrogen	$4{\cdot}61 \times 10^{-23}$	510	$3{\cdot}16 \times 10^{-8}$
Oxygen	$5{\cdot}3 \times 10^{-23}$	480	$2{\cdot}96 \times 10^{-8}$
Mercury	$3{\cdot}31 \times 10^{-22}$	191	$3{\cdot}64 \times 10^{-8}$

Dunoyer's experiment on molecular beams

A vessel is divided into three parts by two walls both provided with a hole in their centre. In the lower part there is a piece of sodium which is heated (Fig. 2.8), after the whole has been exhausted.

Sodium atoms travel in straight paths if the vacuum is good enough for them not to meet residual gas molecules. Then they make a very sharp beam which can be made visible by illuminating it with the yellow light of a sodium vapour lamp (optical resonance). An object put into the beam causes a shadow in its path.

If the pressure gets higher and higher, the beam becomes more and more blurred owing to the decreasing of the mean free path.

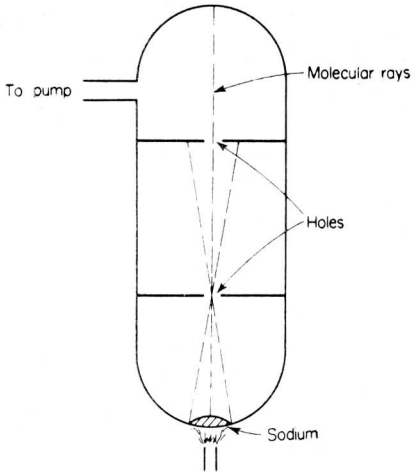


FIG. 2.8

2.2.7. Distribution of molecular concentration of a gas submitted to a field of forces

When the density is changing in terms of a variable (for instance as a function of height, for a gas set in the gravity field), molecular con-

centration is given, at the altitude z, by:

$$\boxed{n = n_0 \, e^{-mgz/kT}} \, , \tag{2.46}$$

where n is the maximum molecular concentration (for $z = 0$). This is known as the *Boltzmann barometric equation.*

In fact, by virtue of Pascal's theorem (statics of fluids), for small variations of pressure and altitude dp and dz, it may be written:

$$dp = -\varrho \, g \, dz. \tag{2.47}$$

But ϱ, the specific mass of the gas, decreases in terms of altitude, since it is equal to:

$$\varrho = n \, m \tag{2.21a}$$

and n decreases when z increases. As, on the other hand, $n = p/k\,T$, the above differential equation becomes:

$$dp = -\frac{p\,m}{k\,T} \, g \, dz. \tag{2.48}$$

Separating the variables and integrating, it follows that:

$$p = p_0 \, e^{-mgz/kT} \tag{2.49}$$

(p_0 = pressure at the ground-level)

so:

$$n = n_0 \, e^{-mgz/kT}. \tag{2.46}$$

Figure 2.9 shows the mean value of the atmospheric pressure, in terms of altitude.

It will be seen, in Vol. II, Chap. VI, that a similar formula is applied to electrons submitted to a retarding electric field.

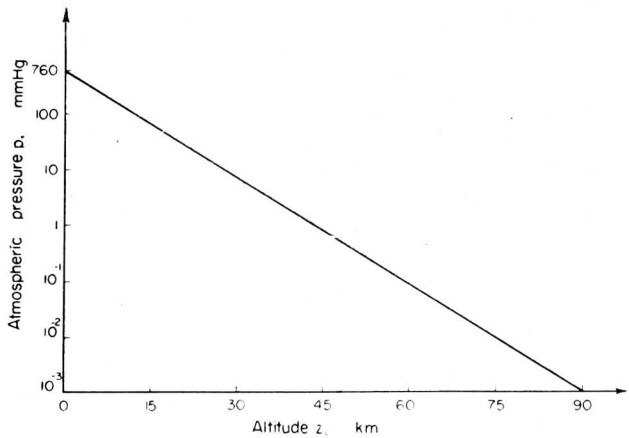


FIG. 2.9. Variation of atmospheric pressure in terms of altitude (average experimental values). Pressure decreases by a factor 10 every 15 km, which corresponds to an average temperature of — 40°C.

2.2.8. Number of collisions on a wall

It has been seen (2.20 a), in the interpretation of pressure according to the kinetic theory, that a wall with a surface S, is struck during an interval of time Δt, by:

$$n_t = \frac{n S u \Delta t}{2} \text{ molecules.} \tag{2.50}$$

As $u = C\sqrt{3}$, the number of collisions per second is:

$$n_t = \frac{n C S}{2\sqrt{3}} . \tag{2.51}$$

Let us replace the root mean square velocity C by the mean velocity v_m. There results, according to (2.40) and (2.42):

$$C = v_m \sqrt{\left(\frac{3\pi}{8}\right)} \tag{2.52}$$

whence:

$$n_t = \frac{n v_m}{4} S \sqrt{\frac{\pi}{2}} . \tag{2.53}$$

This calculation is very simplified. If it had been taken into account that the velocities are not all directed normally to the wall, but that they collide with it in all directions, one would have been led to change $\sqrt{(\pi/2)}$ to 1. Finally, it follows that:

$$\boxed{n_t = \frac{1}{4} n v_m S} . \tag{2.54}$$

2.2.9. Direction of molecular velocities after a collision against a wall

Experience shows that molecules having collided with a wall go off again in directions having no relation with the angle of incidence of the molecules. As it has been assumed by Knudsen, everything happens exactly as if these molecules did not rebound, but remained stuck on the wall for a very short time, and then as if they were "re-evaporated".

The "preferential" direction of velocities after rebound is therefore always the normal to the surface. If x_0 is the number of molecules going off per unit of time and of solid angle along this normal, the number x of molecules going off with any angle α with the normal, is:

$$x = x_0 \cos \alpha \tag{2.55}$$

(analogous to the Lambert law in Optics).

An application of this phenomenon will be seen when studying mechanical molecular pumps.

2.2.10. Flow of gas through an orifice drilled in a thin wall

Let us consider a thin wall separating two vessels A and B with respective pressures p_1 and p_2 ($p_1 > p_2$) and in this wall let us drill a little hole O, with a surface S (Fig. 2.10).

FIG. 2.10

According to eq. (2.54), the mass of the molecules colliding every second a surface S equal to that of the hole, is:

$$\mu = \frac{1}{4} n m v_m S. \tag{2.56}$$

Some molecules go from A to B, and there are some also travelling from B to A, but these are not so numerous, as $p_2 < p_1$.

The resultant mass giving the flow of gas per second through the hole is:

$$\left.\begin{aligned} D_m &= \frac{1}{4} n_1 m v_m S - \frac{1}{4} n_2 m v_m S \\ &= \frac{1}{4} m v_m S (n_1 - n_2) \end{aligned}\right\} \tag{2.57}$$

or, replacing n_1, n_2 and v_m by their expressions in terms of p and T:

$$\boxed{D_m = (p_1 - p_2) S \sqrt{\left(\frac{m}{2 \pi k T}\right)}} . \tag{2.58}$$

This is the *Graham law*. It is also possible to express the flow of a gas in terms of the corresponding volume, measured at the pressure p_1. There results:

$$D_v = \frac{p_1 - p_2}{p_1} S \sqrt{\left(\frac{k T}{2 \pi m}\right)} . \tag{2.59}$$

When $p_1 \gg p_2$, for instance if $p_1 \geq 10\, p_2$, this becomes:

$$D_v = S \sqrt{\left(\frac{k T}{2 \pi m}\right)} . \tag{2.60}$$

In this case, it is seen that the volume (measured under a pressure p_1) of the gas passing through the orifice, is independent of this pressure. In the case of air ($M = 29$), at 20°C and at $p_1 = 760$ mm Hg, with $S = 1$ cm^2, this yields:

$$D_v = 11{,}600 \text{ cm}^3 \text{ sec}^{-1}.$$

2.2.11. Effusion of gases

From what has just been seen, if we compare the flows in volume through an orifice of two gases 1 and 2 at the same temperature, we obtain:

$$\frac{D_{v1}}{D_{v2}} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{M_2}{M_1}} \,. \tag{2.61}$$

This shows that gases pass through a little orifice more easily the lower are their molecular masses.

Experiment. Hydrogen is passed under a bell-jar where there is also a porous vessel made of unglazed porcelain. Hydrogen goes into the vessel quicker than air escapes from it; this is demonstrated by a rough manometer (Fig. 2.11).

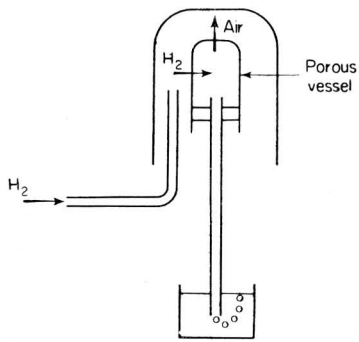


FIG. 2.11

Light gases easily pass through materials insufficiently air-tight: it will be seen later on how easily hydrogen goes through a heated palladium sheet. It is also known that some vacuum tubes using Pyrex bulbs are very slowly filled with atmospheric helium.

Effusion phenomena are used in nuclear physics for separation of isotopes. For this, the substances to be separated are chosen in the form of gaseous compounds which are made to pass through "porous" barriers. The mixture then grows richer in the lighter isotope.

2.2.12. Thermal effusion

Let us consider once more the little hole made through a thin wall (Fig. 2.12).

FIG. 2.12

Now, pressures are supposed to be originally similar, whilst temperatures are supposed to be different, for instance $T_1 > T_2$. Because of the difference of thermal agitation on both sides of the hole, pressures p_1 and p_2 will become different. Let us find out in which way this difference arises.

The mass of gas which moves per sec from A to B is:

$$D_{m1} = \frac{1}{4} m n_1 v_{m1} S. \tag{2.62}$$

Reciprocally, from B to A, there passes per sec:

$$D_{m2} = \frac{1}{4} m n_2 v_{m2} S. \tag{2.63}$$

The resultant mass of gas passing per sec through the hole is then:

$$D_m = D_{m2} - D_{m1} = \frac{S m}{4} (n_2 v_{m2} - n_1 v_{m1}). \tag{2.64}$$

Replacing n and v_m, one obtains:

$$D_m = \frac{S}{4} \sqrt{\left(\frac{m}{2\pi k}\right)} \left[\frac{p_2}{\sqrt{T_2}} - \frac{p_1}{\sqrt{T_1}}\right]. \tag{2.65}$$

This shows that if the little orifice connects together two rooms tight-closed in other respects, gas will come out from the room where the temperature is T_1, to the one where the temperature is T_2 ($T_1 > T_2$), the flow stopping when:

$$\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}. \tag{2.66}$$

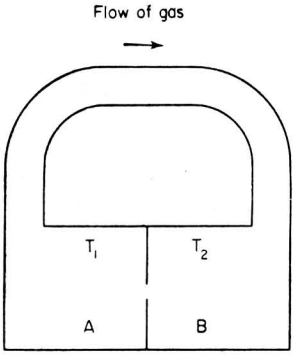


FIG. 2.13

On the contrary, if these two rooms are also connected by a wide section tube, overpressure in room A will more easily come out through this tube than through the little orifice, and a gaseous current in the direction of the arrow will permanently take place, as long as T_1 is higher than T_2 (Fig. 2.13).

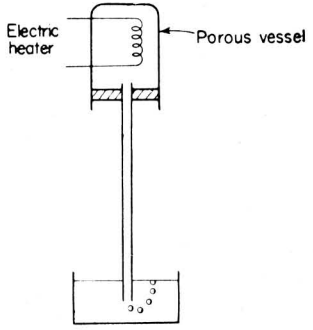


FIG. 2.14

The following experiment† illustrates this phenomenon: a porous vessel made of unglazed porcelain contains a heating resistor and is connected to a water vat by a broad-diameter tube. When the vessel inside is heated, there is a permanent flow of air through the pores, from the atmosphere to the inside of the vessel: this flow is demonstrated by bubbles of air traversing the water of the vat (Fig. 2.14).

† G. A. Boutry, lesson 12 (1).

2.2.13. Specific heat of gases

Since the mean kinetic energy of a molecule is:

$$W_m = \frac{3}{2} k T \tag{2.41}$$

it follows that the mean kinetic energy of 1 g of gas is:

$$U_m = \frac{3}{2} \frac{k}{m} T. \tag{2.67}$$

By definition, the specific heat at constant volume of a gas, c_v, is the quantity of heat to be provided to 1 g *of gas in order to increase its temperature by* 1°C, *the volume being constant.* Specific heat expresses then the rate of variation of the above quantity in terms of temperature, say:

$$c_v = \frac{1}{J} \left| \frac{\mathrm{d}U_m}{\mathrm{d}T} \right|_{v = \text{constant}} = \frac{1}{J} \frac{3}{2} \frac{k}{m} \tag{2.68}$$

(J = mechanical equivalent of the calorie).

2.3. TRANSFER PHENOMENA

Owing to continuous agitation of the molecules of a gas, any modification of its properties is transferred from one point to another of the vessel containing it.

These transfer phenomena will be studied in three cases:

(a) *Viscosity*: This is the property of gases to convey mechanical forces: it relates therefore to an internal friction.

(b) *Thermal conduction*: This is the heat-transfer (therefore kinetic energy transfer) between gas molecules.

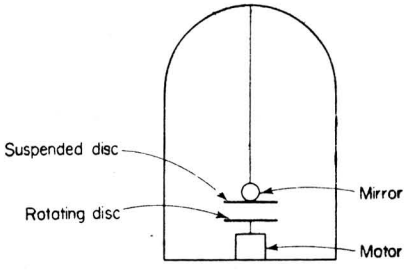


FIG. 2.15

(c) *Diffusion*: This is the fact that two gases brought together mix closely whatever might be their nature, their mass, etc.

2.3.1. Viscosity of gases

Experiment. A horizontal disk rotates around its axis (Fig. 2.15). At a little distance above, a second disk is hung down by a torsion wire.

It is found that the upper disk is driven, which means that it is submitted to a force transferred by gas molecules.

Let x_0 be the distance between the two plates, and v_0 the linear velocity of the lower plate. *It is assumed that gas molecular velocity is varying linearly from* v_0 *to* 0 *when starting from the moving plate to the suspended one*:

$$v = \frac{v_0}{x_0} x. \tag{2.69}$$

The velocity gradient is then:

$$\frac{dv}{dx} = \frac{v_0}{x_0}. \tag{2.70}$$

The frictional force acting on the upper plate and tending to drive it, is proportional to this velocity gradient and to the common surface of the plates:

$$F = \eta S \frac{dv}{dx} \tag{2.71}$$

The coefficient η is *the gas coefficient of viscosity.*

Let us try to connect η to the other parameters of the gas. For that, to simplify matters, every molecule will be supposed to travel between two collisions a path equal to the mean free path L. The distance between the two plates will be separated into gas layers with a thickness L, and it will be assumed that collisions occur only at the limit between the two successive layers (Fig. 2.16). When travelling from one limit to the other of the same layer, the speed variation of gaseous flow is $L\,dv/dx$. In the same circumstances, a molecule of mass m suffers a variation of its momentum equal to $m\,L\,dv/dx$.

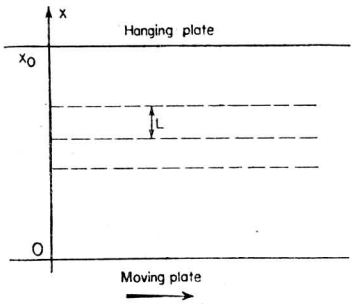


FIG. 2.16

On the other hand, each one of the limits between two layers may be compared to a container wall and correspondingly it may be written that in the direction $O\,x$, they are traversed, per sec, by a number of molecules equal to:

$$n_t = \frac{1}{4} n\, v_m\, S. \tag{2.54}$$

Thus these n_t molecules transfer, every second, from one layer to another, a variation of momentum equal to:

$$n_t\, m\, L\, \frac{\mathrm{d}v}{\mathrm{d}x} = \frac{1}{4}\, n\, v_m\, S\, L\, \frac{\mathrm{d}v}{\mathrm{d}x}\,. \tag{2.72}$$

This expression represents precisely the force F exerted on the successive gas layers and tending to drive them in the moving plate direction. In fact, as:

$$F = \frac{\mathrm{d}\,(m\, v)}{\mathrm{d}t} \tag{2.73}$$

this force is equal indeed to the variation of momentum transferred, per time unit, from one layer to another. Then, we can write:

$$F = \eta\, S\, \frac{\mathrm{d}v}{\mathrm{d}x} = \frac{1}{4}\, n\, v_m\, S\, m\, L\, \frac{\mathrm{d}v}{\mathrm{d}x} \tag{2.74}$$

and obtain:

$$\eta = \frac{1}{4}\, n\, m\, v_m\, L. \tag{2.75}$$

A more accurate calculation taking into account the scattering of individual paths of each molecule would have given:

$$\eta = 0{\cdot}31\, n\, m\, v_m\, L \tag{2.76}$$

or:

$$\boxed{\eta = \frac{0{\cdot}62}{d^2}\sqrt{\left(\frac{m\, k\, T}{\pi^3}\right)}} \tag{2.77}$$

(d = molecule diameter).

This shows that the coefficient of viscosity of a gas is independent of pressure.

TABLE 2.4

COEFFICIENTS OF VISCOSITY AT 0°C

Gas	η
H_2	$0{\cdot}8\times10^{-4}$ CGS
CO_2	$1{\cdot}4\times10^{-4}$ CGS
N_2	$1{\cdot}7\times10^{-4}$ CGS
air	$1{\cdot}7\times10^{-4}$ CGS
O_2	$1{\cdot}9\times10^{-4}$ CGS

Experiment.† A glass tube closed at one end, and at the other end connected to a pump, contains a brass piston able to move in it with gentle friction (Fig. 2.17).

† Fleury and Mathieu (4).

When the piston falls down freely, it is restrained by the air passing between the piston and the glass wall.

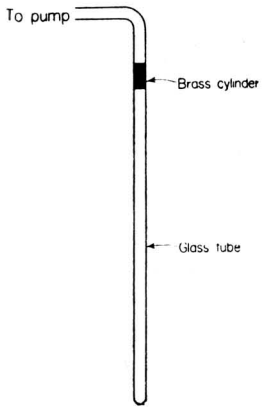


FIG. 2.17

It is found that the falling time for the piston is independent of pressure over a wide range of values (760 to 10 mm Hg approx.).

2.3.2. Thermal conductivity of gases

The phenomenon of heat transfer by conduction in a gas may be calculated as it has been done for viscosity for the transfer of a force.

Let two surfaces A and B be at temperatures T_1 and T_2 respectively (Fig. 2.18). Here again it will be assumed that all molecules travel on a path equal to the mean free path L between two successive collisions. But here, the quantity transferred will be no longer the momentum, but the kinetic energy $m\,v^2/2$.

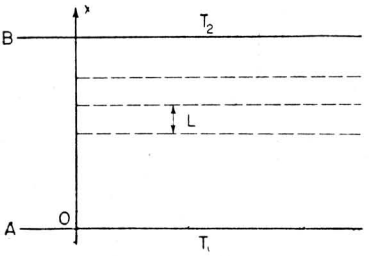


FIG. 2.18

Under these conditions, the quantity of heat transferred, per sec, from one layer to the other, is by definition:

$$Q = \lambda S \frac{\mathrm{d}T}{\mathrm{d}x} \qquad (2.78)$$

the corresponding energy being $J\,Q$ (λ = heat conductivity coefficient of the gas).

But, on the other hand, this kinetic energy is nothing other than the extra kinetic energy acquired by the molecules passing from one layer to the other. For one molecule, it is:

$$L \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{1}{2} m v^2\right) = L \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{3}{2} k T\right) = \frac{3}{2} k L \frac{\mathrm{d}T}{\mathrm{d}x} \qquad (2.79)$$

which gives, for n_t molecules traversing per sec each layer:

$$\frac{3}{2} n_t k L \frac{\mathrm{d}T}{\mathrm{d}x} = \frac{3}{8} k L n v_m S \frac{\mathrm{d}T}{\mathrm{d}x} . \qquad (2.80)$$

Comparing this energy to the energy due to the transferred flow of heat, there is obtained:

$$\frac{3}{8} k L n v_m S \frac{dT}{dx} = J \lambda S \frac{dT}{dx} \tag{2.81}$$

whence:

$$\lambda = \frac{3}{8J} k L n v_m. \tag{2.82}$$

It is also possible to write it as:

$$\boxed{\lambda = \frac{3}{4 J d^2} \sqrt{\left(\frac{k^3 T}{\pi^3 m}\right)}} \tag{2.83}$$

or, using eq. (2.82), (2.68) and (2.75):

$$\lambda = \eta c_v. \tag{2.84}$$

It is seen that the thermal conduction coefficient of a gas is equal to the product of the viscosity coefficient and the specific heat at a constant volume; therefore *it is also independent of pressure.*†

Experiment.‡ A glass bulb connected to a pump contains a metallic filament only slightly oxidizable with a high temperature coefficient of resistivity (e.g. platinum). This filament, electrically heated, dissipates most of its heat by heat-convection (Fig. 2.19).

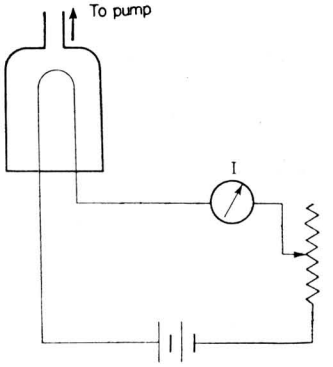


FIG. 2.19

In a wide range of pressures (between 760 and 100 mm Hg roughly), the heating current of this filament remains nearly constant; this proves the constancy of its temperature and correspondingly the constancy of the conduction coefficient of the gas with respect to the pressure.

2.3.3. **Diffusion of gases**

2.3.3.1. *Berthollet's Experiment*

Two glass containers placed one above the other are connected together by a tube divided at its centre by a stop-cock (Fig. 2.20a). The

† As for viscosity, this is true so long as the mean free path remains low in relation to the vessel-dimensions (see Sec. 2.4.1).

‡ Given by L. Dunoyer.

top container is filled with hydrogen, the lower one with carbon dioxide. Then the cock is opened. Owing to large differences of densities (1 to 22), each gas might be expected to remain in its respective vessel. Now, it is found that very soon the two containers are filled exactly with the same mixture of the two gases.

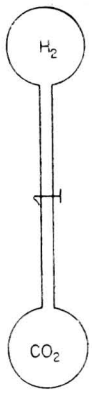


FIG. 2.20a

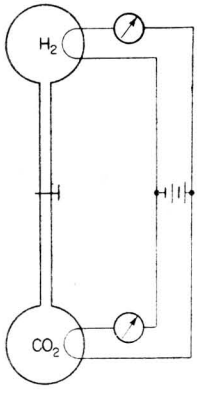


FIG. 2.20b

This may be confirmed by setting in each vessel identical tungsten filaments, supplied from the same electric source (Fig. 2.20b). Before opening the stopcock, the filament of the stop container, strongly cooled by hydrogen, has a lower temperature (and a higher supply power) than that of the filament of the bottom container. After opening the cock, the same quantities become equal for the two filaments.

The two gases have *diffused* each one into the other; this phenomenon is due to thermal agitation of molecules.

2.3.3.2. *Diffusion Coefficient*

For a simpler case, it is originally assumed that the two different gases are at the same conditions of temperature and pressure and contained on either side of a wall separating a long tube at its middle (Fig. 2.21). Let $n = p/kT$ be their mutual molecular concentration. When the wall is removed, the diffusion occurs.

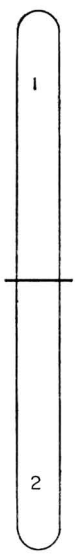


FIG. 2.21

On the side 2, there is a pressure gradient of the gas 1:

$$\frac{dp_1}{dz} = \frac{dn_1}{dz} \tag{2.85}$$

and on the side 1, there is a pressure gradient of the gas 2:

$$\frac{dp_2}{dz} = \frac{dn_2}{dz} \tag{2.86}$$

with at any time:

$$p = p_1 + p_2 \tag{2.87}$$

and:

$$n = n_1 + n_2 \tag{2.88}$$

n being constant, we also have:

$$dn_1 + dn_2 = 0. \tag{2.89}$$

In these conditions, it is evident that if one considers a horizontal plane lying at a distance z from the wall (considered as the origin), the number ν of molecules travelling per sec through this plane (molecular velocity of diffusion) is proportional to the pressure gradient in this place, and consequently proportional to the gradient of molecular concentration:

$$\nu_1 = A_1 \frac{dp_1}{dz} = D_1 \frac{dn_1}{dz} . \tag{2.90}$$

Likewise, we could write:

$$\nu_2 = D_2 \frac{dn_2}{dz} . \tag{2.91}$$

As pressure remains constant, this leads to:

$$\nu_1 = -\nu_2. \tag{2.92}$$

As $dn_1 + dn_2 = 0$, it follows that:

$$D_1 = D_2 = D. \tag{2.93}$$

D is known as the *mutual diffusion coefficient* of the two gases.

It can be calculated, as for viscosity and thermal conduction cases, by dividing the diffusion space into parts equal to the mean free path and writing that the transferred quantity is the molecular concentration of each of the gases. This tedious calculation will not be done here. In the most general cases, i.e. if n and T are different for the two gases, there results:

$$\boxed{D = \frac{L_1 v_{m1} n_2 + L_2 v_{m2} n_1}{3 (n_1 + n_2)}} \tag{2.94}$$

L_1, L_2 = mean free paths,
v_{m1}, v_{m2} = mean velocities,
n_1, n_2 = initial molecular concentrations.

This formula may be simplified in the following cases:

(a) Originally the two gases have the same molecular concentration:

$$n_1 = n_2$$

it follows that:

$$\boxed{D = \frac{L_1 v_{m1} + L_2 v_{m2}}{6}} . \tag{2.95}$$

(b) One of the gases (e.g. gas 2) only exists as traces:

$$n_2 \ll n_1$$

then:

$$\boxed{D = \frac{L_2 v_{m2}}{3} = \frac{2}{3 d^2 p} \sqrt{\left(\frac{k^3 T^3}{\pi^3 m}\right)}} \,. \tag{2.96}$$

(c) One has only to deal with the same gas diffusing in itself (mixture of various isotopes of a same gas) e.g.:

$$\boxed{D = \frac{L v_m}{3} = \frac{\eta}{\varrho}} \tag{2.97}$$

(η = viscosity coefficient; ϱ = specific mass).

Formula (2.96) shows that if two gases diffuse into a third one, their diffusion velocities are inversely proportional to the square root of their molecular masses:

$$\frac{v_1}{v_2} = \frac{D_1}{D_2} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{M_2}{M_1}} \,. \tag{2.98}$$

An important application of these principles will be seen when studying diffusion-pumps (Chap. V).

2.4. ELEMENTS OF DYNAMICS OF GASES

Until now it has been assumed that, although each molecule moves by its natural movement, the mass of gas considered was free of a combined movement.

Now we shall study what occurs when the whole gaseous mass is moving with respect to the walls of the containing vessel. The most interesting point will be phenomena of gas flow through pipes.

In the following development, the flow will be supposed to be laminary (non-turbulent), which means that vortices do not occur in the moving gas.

2.4.1. Existence of two kinds of gas flow

Reference will be made to the experiment of Fig. 2.15. The independence on pressure of the viscosity coefficient and the forces connected with it, is confirmed only if the distance between the two plates is large compared with the mean free path. If it is not so, i.e. if the pressure is very low, collisions between molecules will be few in comparison

with collisions against the walls, and the viscosity coefficient decreases in terms of pressure, when the mean free path becomes high compared with the space between the plates (Fig. 2.22).

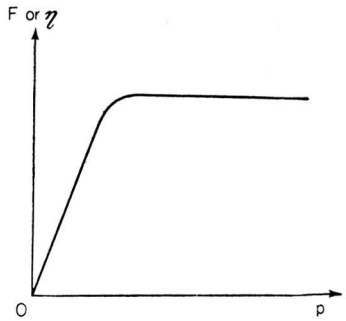


FIG. 2.22

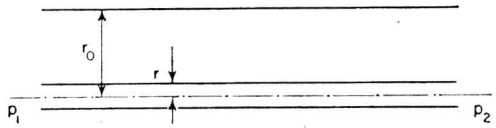
Then it may be deduced that the flow of gas inside a pipe, according to the circumstances, may follow two different laws:

(a) *Viscous (or Poiseuille) flow.*

In this case, the pressure is high enough for the mean free path to be small compared with the diameter of the pipe: the number of collisions between the molecules is then high compared with the number of collisions of the molecules against the walls.

(b) *Molecular (or Knudsen) flow.*

In this case, the pressure is low enough for the mean free path to be large compared with the diameter of the pipe: the number of collisions between molecules is then small compared with the number of collisions of the molecules with the walls.†



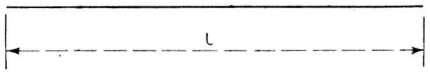


FIG. 2.23

2.4.1.1. *Viscous (or Poiseuille) Flow*

Let a pipe be of length l and constant radius r_0. The purpose is to calculate the flow through this pipe under a difference of pressure (or load-loss) $p_1 - p_2$ $(p_1 > p_2)$.

Consider a small element of a column of gas centred on the axis (Fig. 2.23).

When the flow has reached a steady rate, the forces acting on this gas column must balance each other. They are of two kinds:

(a) the motive force due to the difference of pressure $p_1 - p_2$ and which is the product of $p_1 - p_2$ by the section of the element:

$$f_1 = (p_1 - p_2)\,\pi\, r^2, \tag{2.99}$$

† A pipe of which the diameter is small enough so that this condition may apply, is known as a *capillary pipe.*

(b) the resisting force due to frictional viscosity, the value of which is, as has been seen above:

$$f_2 = \eta S \frac{dv}{dx} . \tag{2.100}$$

S is the lateral surface of the element considered, and v is the translational velocity of the gas; dx has to be changed into dr; whence:

$$f_2 = 2\pi \eta r l \frac{dv}{dr} . \tag{2.101}$$

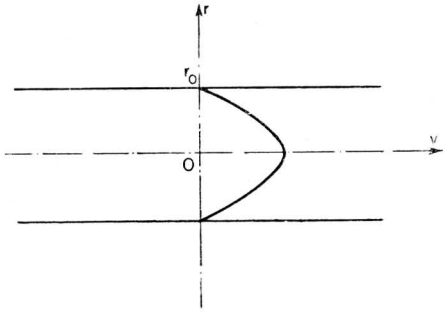


FIG. 2.24

Equilibrium requires $f_1 = f_2$, whence:

$$(p_1 - p_2)\pi r^2 = 2\pi \eta r l \frac{dv}{dr} . \tag{2.102}$$

Or, further:

$$(p_1 - p_2)\frac{r}{2} = 2\pi \eta l \frac{dv}{dr} . \tag{2.103}$$

By integration, we obtain:

$$(p_1 - p_2)\frac{r^2}{2} = 2\eta l v + \text{constant}. \tag{2.104}$$

The constant is deduced by assuming that $v = 0$ for $r = r_0$. Whence:

$$v = \frac{(p_1 - p_2)(r_0^2 - r^2)}{4\eta l} . \tag{2.105}$$

It is pointed out that the law for the variation of the velocity in terms of the radius is a parabola (Fig. 2.24). Flow in volume, calculated for a mean pressure in the pipe:

$$p = (p_1 + p_2)/2 \tag{2.106}$$

will be given by:

$$D_v = \int_0^\infty v\, 2\pi r\, dr = \frac{\pi r_0^4}{8\eta l}(p_1 - p_2). \tag{2.107}$$

As to the mass flow, it is equal to:

$$\boxed{D_m = D_v \varrho = \frac{\pi r_0^4}{8\eta l}(p_1 - p_2)\, p \frac{M}{R T}} . \tag{2.108}$$

2.4.1.2. *Molecular (or Knudsen) Flow*

It is known that in this case the mean free path is greater than the pipe diameter.

The forces balancing are, on the one hand, the motive force (expressed on the whole section of the tube):

$$f_1 = (p_1 - p_2)\,\pi\, r_0^2 \tag{2.109}$$

and, on the other hand, the resisting force, equal to the momentum transferred per sec to the wall, of all the molecules colliding with it:

$$f_2 = S\, n_t\, m\, v. \tag{2.110}$$

n_t is the molecule number striking 1 cm² of wall per sec, S is the surface of the latter and v is the translational velocity of the gas in the pipe.

Now the number of collisions against the wall per sec and per cm² is, according to eq. (2.54):

$$n_t = \frac{1}{4}\, n\, v_m \tag{2.111}$$

whence:

$$f_2 = \frac{\pi}{2}\, r_0\, l\, m\, n\, v_m\, v. \tag{2.112}$$

Therefore it must be obtained, at equilibrium $f_1 = f_2$, or:

$$(p_1 - p_2)\,\pi\, r_0^2 = \frac{1}{2}\,\pi\, r_0\, l\, m\, n\, v_m\, v. \tag{2.113}$$

The velocity of the gas, constant at every point of radius, is deduced as:

$$v = \frac{2\, r_0}{l\, m\, n\, v_m}\,(p_1 - p_2) \tag{2.114}$$

or:

$$v = \frac{r_0\,(p_1 - p_2)}{l\, p}\,\sqrt{\left(\frac{\pi\, R\, T}{2\, M}\right)}. \tag{2.115}$$

p being still the mean pressure:

$$p = \frac{p_1 + p_2}{2}.$$

The flow in volume, measured at this mean pressure, is:

$$D_v = \pi\, r_0^2\, v = \frac{\pi\, r_0^3\,(p_1 - p_2)}{l\, p}\,\sqrt{\left(\frac{\pi\, R\, T}{2\, M}\right)}. \tag{2.116}$$

This calculation is not accurate because all the molecules have implicitly been supposed to strike the walls normally. In fact, π must be changed by 8/3:

$$D_v = \frac{8\, r_0^3\, (p_1 - p_2)}{3\, l\, p} \sqrt{\left(\frac{\pi\, R\, T}{2\, M}\right)} . \qquad (2.117)$$

As for the mass flow, this is equal to:

$$D_m = D_v\, \varrho = D_v \frac{p\, M}{R\, T} = \frac{8}{3} \frac{r_0^3\, (p_1 - p_2)}{l} \sqrt{\left(\frac{\pi\, M}{2\, R\, T}\right)} . \qquad (2.118)$$

2.4.1.3. *Comparison of the Two Kinds of Flow*

In both cases, the mass flow is proportional to the load-loss and inversely proportional to the tube length.

The following differences are noted between the two kinds:

(a) The flow of gas is proportional to the fourth power of the pipe radius with viscous flow, and to the third power with molecular flow.

(b) The mean pressure in the pipe and the gas viscosity do not enter into viscous flow.

(c) Variations of the molecular mass of the gas and of temperature have a greater effect in viscous flow than in molecular flow.

We shall see some important applications of these formulae in the calculation of low-pressure pipes (Chap. VII).

2.4.2. **Fluid flow in pipes with varying diameter**

We shall see that certain pumps use a phenomenon of entraining gas by viscosity (therefore in viscous flow) with the help of fluids moving at a high speed in pipes, the diameter of which varies from one point to another.

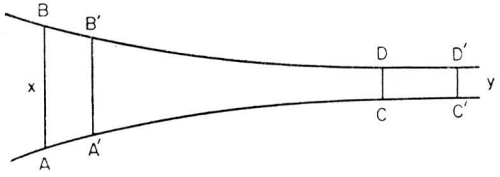


FIG. 2.25

2.4.2.1. *Bernouilli Formula*

For simpler calculations, suppose one has to deal with an incompressible fluid (a liquid). The conclusions may apply to the case of a compressible fluid (a gas), though the formula is not strictly the same. Consider a pipe $x\, y$, with a variable diameter, in which the liquid is

supposed to be in "stationary" motion, i.e. that at each point speeds are independent of time (Fig. 2.25).

The influence of the wall on the fluid velocity will be neglected, so that speed will be assumed to be the same at all points of the same straight section.

Let s_1 be the surface of the section AB, where the speed is u_1. The volume supplied per sec is $s_1 u_1$. The fluid being supposed incompressible, this volume is constant, and, e.g. in CD, we have:

$$s_2 u_2 = s_1 u_1. \tag{2.119}$$

After a time dt, the fluid originally in AB came to $A'B'$, and that which was in CD came to $C'D'$, with:

$$AA' = dx_1 \quad \text{and} \quad CC' = dx_2.$$

As:

$$dx/dt = u$$

whence:

$$s_1 dx_1 = s_2 dx_2. \tag{2.120}$$

During this time dt, the work done by the forces due to pressure is:

$$W = p_1 s_1 dx_1 - p_2 s_2 dx_2. \tag{2.121}$$

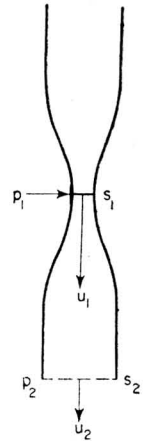


FIG. 2.26

Then, applying conservation of energy, this work is equal to the kinetic energy variation of the fluid mass:

$$p_1 s_1 dx_1 - p_2 s_2 dx_2 = \frac{1}{2} \varrho s_1 dx_1 (u_2^2 - u_1^2) \tag{2.122}$$

whence:

$$\boxed{p_1 - p_2 = \frac{1}{2} \varrho (u_2^2 - u_1^2)} \; . \tag{2.123}$$

This is the *Bernouilli formula*, connecting pressure variation with speed variation of a fluid, friction being neglected.

2.4.2.2. *Venturi's Paradox*

A fluid passes with a certain speed through a pipe provided with a restriction. Let s_1 and u_1 be the restricting section and the corresponding speed respectively; and s_2, u_2 the corresponding values at the enlarged part through which the fluid escapes (Fig. 2.26). According

to the above equation, and as $s_2 u_2 = s_1 u_1$ we may write that:

$$p_1 = p_2 - \frac{1}{2} \varrho u_2^2 \left[\frac{s_2^2}{s_1^2} - 1 \right] . \qquad (2.124)$$

The pressure p_1 at the restriction may thus be appreciably lower than p_2 at the outlet: this is *Venturi's paradox*. For instance, if a part of the restricting wall were elastic, it might be drawn inside the pipe.

2.4.2.3. *Applications*

In vacuum technique: the water-jet pump, the steam-jet ejector (see Chap. V).

In gas dynamics: the Pitot tube and the Venturi flowmeter are used respectively to measure the speed and the magnitude of the flow of a gas.

On locomotives, the Giffard injector uses a steam-jet to supply the boiler with water coming from the tender.

Burners of gas ovens and gas lighting lamps use the underpressure caused by the passage of a gas through a restriction to draw in the air required for combustion.

On the other hand, spray-guns and vaporizers use the fall in pressure produced by an air-jet to suck up the liquid to be atomized.

CHAPTER III

FLOW OF ELECTRIC CURRENT THROUGH GASES

IT WILL be seen later that some manometers and pumps utilize ionization phenomena. Many kinds of electron tubes use a gas atmosphere at a rather high pressure. Even in "vacuum tubes", residual gases remain, the ionization of which sometimes causes troublesome disturbances. For all these reasons, it is necessary here to review elementary principles governing the passage of electric currents through gases.

3.1. NATURE OF ELECTRICITY

It is well known that negative electricity appears to play a particularly important part: thermionic and photoelectric phenomena, radioactivity and cathode rays, showed that matter may give off negative charges independent of any material base.

3.2. THE ELEMENTARY CHARGE. THE ELECTRON

The Millikan Experiment. Under a bell-jar which is partially exhausted, some drops of oil are evaporated between two plates shaped like a capacitor. The system is lit from the side, and one of the drops is watched with a microscope. It falls owing to gravity action. The force applied on the drop is $f = mg$. The fall is slowed down by gas viscosity (Fig. 3.1).

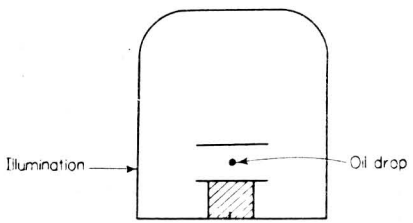


FIG. 3.1

Let us apply a potential difference V between the two plates. If the drop is electrically uncharged, nothing is changed in its motion. If it carries a charge $+Q$, it is subjected by the electric field to an extra force:

$$\pm F = \pm EQ = \pm \frac{V}{l} Q \tag{3.1}$$

(l is the distance between the two plates and E the electric field). The direction and magnitude of V may be adjusted so that the drop remains still, i.e. $F = -f$. It then results that:

$$\frac{V}{l} Q = -m g. \tag{3.2}$$

It is then observed that all the charges Q of the drops able to be studied are integral multiples of a certain quantity e, known as the elementary charge:

$$e = 1{\cdot}6 \times 10^{-15} \text{ Coulomb}.$$

Electrical particles carrying this charge are called *electrons*. Their mass is equal to:

$$m = 9{\cdot}1 \times 10^{-31} \text{ kg}$$

or 1/1830 of the mass of the hydrogen atom.

When an electron originally at rest is set in an electric field, it moves towards increasing potentials. To move it between two points submitted to a potential difference of 1 V, an energy of 1 *electron-volt* has to be supplied, which is equal to:

$$1 \text{ eV} = 1{\cdot}6 \times 10^{-19} \text{ Coulomb} \times 1 \text{ V} = 1{\cdot}6 \times 10^{-19} \text{ Joule}$$
$$= 1{\cdot}6 \times 10^{-12} \text{ erg}.$$

This energy is stored by the electron as kinetic energy.

Inversely, the electron will be able to move against a retarding field of 1 V only if it has a velocity at least corresponding to a kinetic energy of 1 eV.

As a general rule, between the mass, the speed and the charge of a particle on one hand, and the potential on the other, the following identity may be written:

$$m v^2/2 = eV. \tag{3.3}$$

When there is no ambiguity, it is also said that an electron has acquired or given up *an energy of V volts*.

3.3. CLASSICAL THEORY OF THE ATOM (BOHR SYSTEM)

The scientists Bohr and Rutherford have been led to conceive the following pattern for an atom:

In the centre, a *nucleus*, positively charged, carries nearly the whole mass of the atom. One or several electrons carrying negative charges

revolve around it. *The nucleus charge is such that the whole charge of the atom is zero* (Fig. 3.2).

The atom of hydrogen† has only 1 electron, the helium one has 2, the lithium one has 3, etc. In a general way, *an atom includes as many electrons as is indicated by its atomic number Z or its place in the Mendeleev periodic table* (see Appendix II). An atom is entirely defined by two numbers put at the left of its symbol. The top one is the atomic mass M, and the lower one is its atomic number Z:

$$^{40}_{18}\mathrm{A}\ (\text{argon}).$$

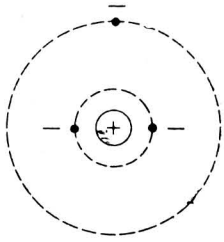


FIG. 3.2

Electrons are distributed in one or several orbits denoted, from inside to outside, by letters K, L, M, N, O, P.

Table 3.1 gives, for example, the electron distribution in the different orbits, for the inert gases.

TABLE 3.1

Atomic number	Element	Number of electrons in complete orbits					
		K	L	M	N	O	P
2	He	2					
10	Ne	2	8				
18	A	2	8	8			
36	Kr	2	8	18	8		
54	Xe	2	8	18	18	8	
86	Rn	2	8	18	32	18	8

Electrons cannot remain motionless, because then they would fall on the nucleus, being attracted by the Coulomb attraction-force. Therefore they must rotate round the nucleus to have a centrifugal force in opposition to the first one.

However, in classical mechanics, this could be obtained with any orbit; *on the contrary in the case of the atom, only certain orbits are allowed.*

† The hydrogen atom nucleus is known as the *proton*.

On the other hand, *for a given atom, one single arrangement of the orbits corresponds to a stable configuration*: it may occur that under the influence of an external cause (e.g. a collision with another particle), an electron might be shifted from one orbit to other; but, in this case, it will not take long to come back again to its normal position, *giving back, in the form of radiation, the energy with which it has been provided.*

Stability of orbits is maximum for a certain number of electrons. Regarding the electrons of the external layer (the farthest from the nucleus), known as *optical, valence* or *conductivity* electrons (because they are responsible for optical, chemical or electrical phenomena), maximum stability occurs with 8 electrons, except in the case of one single layer which can only keep 2. In no case, for a neutral atom, may there be more than 8 electrons in this external layer, but it may be less than that (in the case of chemically active materials).

For instance, inert gases, chemically passive, include complete external orbits (2 or 8 electrons).

An atom having a small number of external electrons will have a tendency to lose them, thus becoming positively charged: it is said to be *electropositive* (e.g. alkali elements). An atom possessing many external electrons (but less than 8), will have a tendency to pick up some more in order to reach this number 8; in this way it will become negatively charged: it is said to be *electronegative* (e.g. halogen elements). It follows that electropositive and electronegative elements have an affinity for each other. For instance: sodium (one external electron) has an affinity for chlorine (7 external electrons).

3.4. ENERGY REQUIRED TO DISPLACE AN ELECTRON REVOLVING ROUND A NUCLEUS

This energy is separated into two kinds: kinetic and potential energies.

(a) *Kinetic energy*

Located at a distance r from the nucleus, an electron is submitted to a Coulomb attraction force:

$$f = e^2/r^2. \tag{3.4}$$

Revolving round its orbit with a speed v, it is submitted to a centrifugal acceleration:

$$\gamma = v^2/r. \tag{3.5}$$

From:

$$f = m\gamma \tag{3.6}$$

this may be written as:

$$e^2/r^2 = m\,v^2/r. \tag{3.7}$$

The kinetic energy of the electron is then equal to:

$$W_c = m\,v^2/2 = e^2/2\,r. \tag{3.8}$$

At infinity this energy is zero.

When the electron is taken from r to infinity, it *liberates* an energy equal to the above value.

(b) *Potential energy*

The field created by the nucleus at the place where the electron is lying, is equal to:

$$E = e/r^2. \tag{3.9}$$

The field is derived from a potential:

$$V = -e/r. \tag{3.10}$$

The potential energy of an electron lying at a distance r from the nucleus is then equal to:

$$W_p = eV = -e^2/r. \tag{3.11}$$

The sign $-$ means that to carry the electron from the distance r to infinity it *absorbs* from the external medium (and stores under potential energy) an energy equal to the above value.

(c) The *total energy* to take into account in the removal of an electron from r to infinity is then:

$$W_t = W_c + W_p = -e^2/2\,r. \tag{3.12}$$

The result is that, to remove an electron, it is necessary to *supply* energy from the external medium.

3.5. PRODUCTION OF RADIATION

Inversely, we can see, owing to the above value of W_t, that *if an electron moves from a remote orbit (or from infinity) to a near orbit, it supplies (or gives back) energy, which appears under the form of radiation.*

Suppose that after a collision, an electron has received from the outside medium energy allowing it either to leave the atom entirely or to go from a near orbit to a remote one.

In the first case (total separation), the process is called *ionization*.

In the second case (change of orbit), the process is called *excitation*.

In both cases, the atom will endeavour to come back to its stable state, and during this operation, the electron will give back an energy W, under the form of a light radiation (visible or invisible), the frequency of which ν, is related to this energy by the fundamental following equation:

$$\boxed{W = h\nu} \cdot \tag{3.13}$$

This is the *Einstein relation*.

h is the action quantum, or Planck constant and is equal to $6{\cdot}62 \times 10^{-34}$ J. s, when W is in Joules and ν in hertz (cycles per second).

Owing to the fact that electron orbital radii are not arbitrarily determined, but vary by finite quantities, it is said that one deals with a "*quantized phenomenon*".

The quantity $h\nu$ is considered as the energy of a corpuscle of light, and is called a *photon*.

3.6. IONIZATION

The removal of an electron from an atom, or its transfer from one orbit to another, may be due to several causes:

3.6.1. **Ionization by collision**

By injecting fast particles into a gas, its atoms may be ionized: this is the case of electrons emitted by a hot cathode, when they are suitably accelerated; it is also the case for α and β rays emitted by radioactive materials.

Thus, calling W_i the work required to remove an electron from an atom, the speed of the particles must be such that:

$$m v^2/2 > W_i. \tag{3.14}$$

The energy W_i is called *ionization energy*, and the corresponding potential $V_i = W_i/e$ is the gas *ionization potential*.

The radiation produced by the atom when it comes back to its

initial state has a frequency defined by the equation:

$$h\nu = W_i = e V_i = m v_0^2/2 \tag{3.15}$$

v_0 being the precise speed which particles must possess to bring about ionization.

It can also be seen that in a gas-tube, *ionization cannot happen if electrons are accelerated to a voltage lower than* V_i.

The wavelength λ (measured in angstrom units†) of the radiation produced is related to the ionization potential by the formula:

$$\lambda = \frac{12{,}400}{W_i}, \tag{3.16}$$

where W_i is taken in e V.

3.6.2. **Ionization by absorption of radiation**

Not only material particles may eject an electron from an atom. Any radiation may do it, so long as its energy is sufficient. This is the case for γ, X or ultra-violet rays. Here again, the condition for ionization to occur is that:

$$h\nu \geq W_i \tag{3.17}$$

or:

$$\lambda \leq \frac{12{,}400}{W_i}. \tag{3.18}$$

Visible light cannot produce ionization.‡ In fact, the gas having the lowest ionization energy is caesium vapour ($W_i = 3{\cdot}88$ eV). Thus to ionize it, a radiation with a wavelength lower than 3184 Å is required, which is an invisible ultra-violet radiation.

When the quantum energy $h\nu$ of the radiation is greater than the ionization energy, the extra energy is supplied to the extracted electron as kinetic energy, so that the following relation is fulfilled:

$$h\nu = W_i + m v^2/2 \tag{3.19}$$

(v is then the speed with which the electron leaves the atom from which it is ejected).

† 1 angstrom unit (Å) = 10^{-10} m.

‡ It can be recalled that visible light has wavelengths included between about 4000 and 7000 Å.

If this velocity is high enough, the expelled electron may in turn ionize other atoms by collision. This is what occurs with powerful radiations ($h\nu$ high, consequently λ small: γ or X-rays).

3.6.3. **Ionization by high-frequency fields**

This is only another aspect of ionization by collision: if a sealed tube, containing a low-pressure gas, is set in an h.f. field, the few free electrons existing in this gas begin to oscillate and if their amplitude is sufficient, they may ionize the gas.

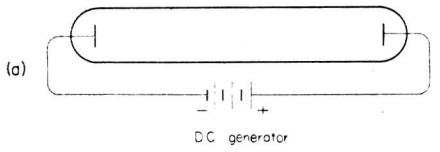


FIG. 3.3a

But whilst with a continuous or alternating low frequency potential difference, electrodes are required to be in contact with the gas (Fig. 3.3a), on the contrary with an h.f. potential difference, external electrodes are sufficient (Fig. 3.3b), the current flowing by capacity.

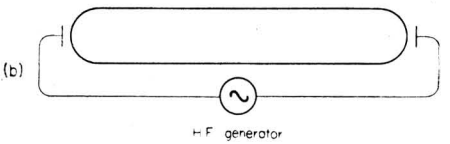


FIG. 3.3b

3.6.4. **Thermal ionization**

If an alkaline atom falls on a metal suitably chosen and heated, it is found that the atom gives an electron to the metal and goes away again in the shape of a positive ion. To this phenomenon, studied by Langmuir in 1920, certain ionization phenomena noted in stellar atmospheres can be imputed; it is now on the way to various applications.†

The best results, i.e. the highest ratios between ions produced and molecules colliding with the target, are obtained by using as targets, metals with a high work function (see Vol. II, Chap. III) (platinum, tungsten, molybdenum), and as gases, alkaline vapours with a low ionization potential (caesium, potassium, sodium, etc.).

† Flame-gases are ionized: it is easily proved by heating a glass rod in a Bunsen burner: a yellow glow appears, which is characteristic of the line 5890 Å of sodium.

3.6.5. Table of ionization potentials and maximum wavelengths

TABLE 3.2

Gas or vapour	V_i (volts)	λ max (Å)
Cs	3·88	3184
K	4·32	2850
Na	5·1	2410
Hg	10·4	1187
O_2	12·6	978
H_2	13·5	913
N_2	14·5	850
He	24·5	502
Ne	21·5	574
A	15·7	786
Kr	14	880
Xe	12·1	1029
Rn	10·7	1150

Concerning inert gases known to have complete external orbits, it will be noticed that ionization potentials decrease as atomic number increases, therefore proportionately as the diameter of the external orbit increases.

This happens, in fact, because the forces binding the electron to the nucleus decrease when the distance from the one to the other rises (after Coulomb law).

3.7. EXCITATION

When the energy of electrons or of radiation which act on the gas is too low to produce ionization, it may, however, move an electron from its orbit to another more remote. This phenomenon, known as *excitation*, requires less energy than that properly called ionization.

An electron coming back to its normal orbit is also accompanied with light emission governed by the Einstein relation.

3.8. INTERMEDIATE LEVELS — METASTABLE STATES

All the electrons expelled or transferred by ionization or by excitation do not come back necessarily in one single jump to their resting point. They may temporarily settle upon one or several intermediate

orbits. The different energy levels which an atom may encounter during ionization or excitation are usually illustrated by horizontal straight lines of which the distance to the origin (non-excited atom) is proportional to the corresponding energy (*energy levels diagrams*) (Fig. 3.4).

Some of these levels correspond to energies which are never to be taken into account in absolute value (i.e. when they are considered as measured from zero), but which appear in relative values (i.e. when

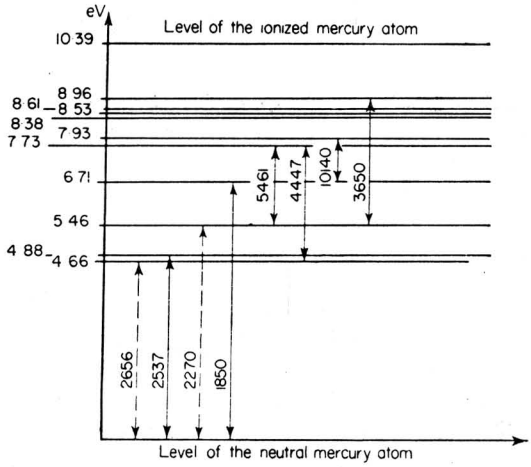


FIG. 3.4

differences are considered in relation to another level). These are called the *metastable states* of the atom: when this latter radiates, radiations corresponding to the absolute level of their energy never appear (dotted lines in Fig. 3.4).

On the other hand, the excitation levels from which the atom comes back directly to its zero state are known as *resonance levels.*

3.9. IONIZATION AND DEIONIZATION TIME CONSTANTS

The expulsion or the transfer of an electron, though non-instantaneous, occurs in a very short time: 10^{-6} to 10^{-7} sec.

When a gas has been ionized and when the cause of ionization ceases, a rather longer time is required for atoms to collect up free electrons, or for shifted electrons to come back to their previous orbits.

This time is the longer as the atom is more complex, i.e. as the atomic number is higher. This deionization time is about 10^{-3} sec for mercury and about 10^{-5} sec for hydrogen. This imposes a limit to gas-tube working at high frequencies.

For instance, it will be seen (Vol. II, Chap. XI) that ordinary thyratrons cannot perform successive firings and extinctions repeated at intervals corresponding to more than some tens of thousands cycles per sec.

However, adding small quantities of oxygen to a gas reduces its deionization time. This is due to the following fact:

Whilst most gases give by ionization only positive ions, the oxygen atom may collect an electron to produce a negative ion. These ions promote a fast recombination of ionized gas elements. This property is applied in duplexer tubes used in radar, which must have a very low deionization time (see Vol. II, sec. 11.1.3).

3.10. COLLISIONS BETWEEN ATOMS AND ELECTRONS

3.10.1. Mean free path of electrons through a gas

If the calculation for atomic mean free path (Sec. 2.2.6) is considered again in the case of electrons, it can be found that the mean free path of electrons travelling in a gaseous atmosphere is given by:

$$L_e = \frac{4}{\pi d^2 n} = \frac{4 k T}{\pi d^2 p} \quad . \tag{3.20}$$

This results in a mean free path $4\sqrt{2}$, or 5·6 times higher than the atomic ones. It is to be noticed that d represents here again the diameter of the atom and not the electron.

3.10.2. Probability of collisions

Of course, electrons flowing in a gas have not a probability of unity to collide with an atom. This probability is easily calculated by dividing the total distance travelled by the mean free path.

EXAMPLE. In a thyratron in which the electron mean free path is 35 cm, and the cathode-to-anode distance is 3·5 cm, on an average there will be 1 collision for 10 electrons flowing from the cathode to the anode.

This calculation is only accurate when the mean free path is great in comparison with the distance travelled by the electrons.

3.10.3. **Ionization probability**

Furthermore, all the collisions are not necessarily followed by an ionization of the collided atom. That depends evidently on the way the atom is struck, and on the place of the electrons in the external layer of the orbit at the instant of the collision. Only experimental studies may be done on that subject, the results of which are given on Fig. 3.5.

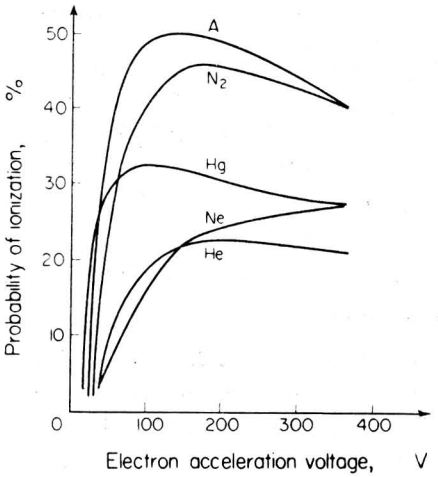


FIG. 3.5

We may ascertain the following points:

(a) The ionization probability (probability in % for the collision of an electron with an atom to produce one ion) is zero for an electron energy inferior to the ionization potential, and increases at first according to a nearly linear law.

(b) The ionization probability passes through a maximum, and then decreases for high energies.

(c) The maximum occurs for an energy which is nearly about the same for all gases and lies between 100 and 150 V.

(d) The maximum probability is the higher, the greater the diameter of the atom.

The existence of the maximum is explained by assuming that at low speeds the electron (negative) has a chance to be attracted by the nucleus (positive), which makes the collision easier; at high speeds, these chances decrease.

Another way of conceiving the ionization probability of a gas consists in drawing the curve of its *specific ionization coefficient* in terms of the energy of incident electrons: this deals with the mean number of ions produced by each electron per cm of path (Fig. 3.6).

3.11. ENERGY OF PARTICLES CONSTITUTING THE PLASMA

In an ionized gas, the complex medium composed of neutral atoms, ions and electrons is named the *plasma*.

Without any electric field, the average energy of all the plasma particles, whatever may be their charge or their mass, is given by the kinetic theory of gases:

$$W_m = \frac{3\,k\,T}{2} \,. \tag{2.41}$$

This is also the energy which an *electron gas* would have, that is a gas composed only of electrons issuing from a cathode at a temperature T.

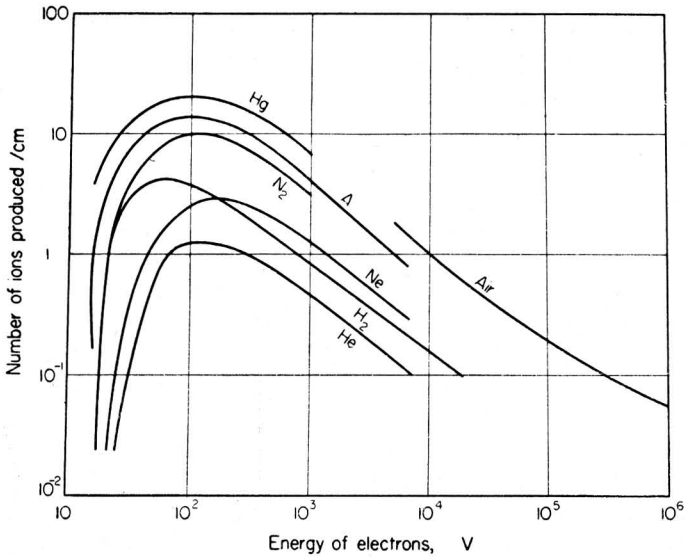


FIG. 3.6

If the plasma is subjected to an electric field produced by a potential difference V, only ions and electrons are accelerated. They acquire an extra kinetic energy (see also Vol. II, Chap. I):

$$W_c = e\,V \tag{3.3}$$

e being their charge.

It is then easy to calculate the temperature which the gas must reach so that the particles have, by thermal agitation, this same energy. It is readily found equating (2.41) and (3.3):

$$W_m = W_c = \frac{3}{2} k T = e V. \tag{3.21}$$

In the case of electrons, this gives:

$$T = 7730 V \tag{3.22}$$

taking V in volts.

This shows how electrons accelerated under 1 V acquire an energy they should reach by thermal agitation only at a temperature of 7730°K.†

3.12. STUDYING THE CURRENT IN TERMS OF THE VOLTAGE IN THE GASEOUS DISCHARGE

Consider the following circuit:

Connect a voltmeter across a bulb containing a gas at a low pressure and provided with two electrodes. In series, set an ammeter, a protecting resistor R and a d.c. generator G, supplying an adjustable voltage (Fig. 3.7).

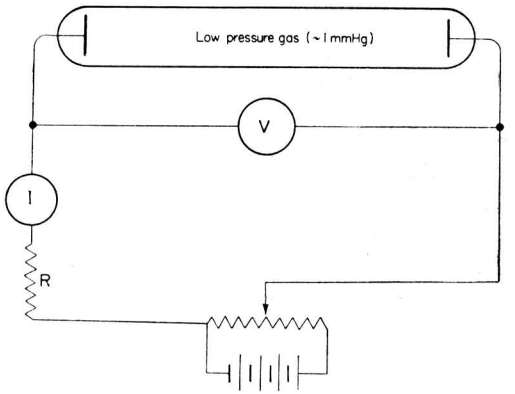


FIG. 3.7

Initially the voltage is zero and it will be increased progressively. Plot the curve $I = f(V)$ (Fig. 3.8).

(a) First a range OA is found in which the current (very small) increases in terms of the applied voltage. This current is due to the *electrical conduction of the gas*, because, owing to *natural causes of ionization* (surrounding radioactivity, cosmic rays, ultra-violet rays), some

† This enables us to understand how it is possible to obtain the extremely high plasma temperatures required to realize the *fusion of heavy hydrogen molecules*, in order to produce *thermonuclear energy*.

ions and electrons are produced in the gas. When they are all collected, the current reaches saturation (range AB).

In the range OAB, the electric discharge (invisible) is called a *non-self-maintained discharge*: in fact it would stop if natural ionizing causes were suppressed.

(b) If we continue to increase the voltage, the current again begins to rise. This is due to the fact that the collected ions and electrons are accelerated and that they ionize gas molecules by collision: hence

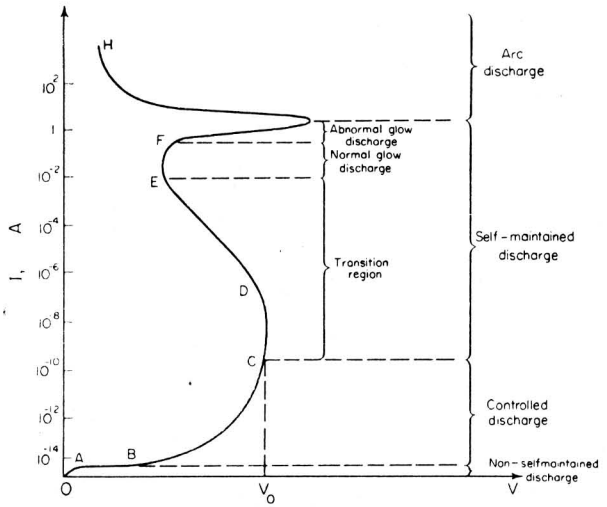


FIG. 3.8

the current keeps increasing. This "amplification" is used in gas-filled photo-cells and in Geiger-Müller counters (see Vol. II, Chap. XI). However, the natural causes of ionization remain essential to produce the discharge: whence the name of *controlled discharge* given to this region BC. In this case a low light-emission starts to occur.

(c) As soon as the voltage reaches the value V_0 corresponding with the point C, the current suddenly increases by several orders of magnitude. The voltage V_0 is known as the *breakdown potential*. This phenomenon is due to the fact that the energy and the number of the ions are sufficient to maintain the discharge in the gas without any *external causes*. The light emission becomes important. The current cannot be stabilized in the range CDE, corresponding to an internal resistance

zero or negative. It stabilizes at E, and at the same time, due to the existence of the resistor R, the voltage across the tube is fixed to a corresponding value.

(d) From E to F, the internal resistance of the tube is positive again; therefore this region is stable: it is the region of the *normal glow discharge*, in which luminescent tubes work. Though the internal resistance is positive, it is very low. The current increases rapidly for a small increase of V: this effect is used in neon stabilizer tubes (see Vol. II, Sec. 11.1.2). At E only a little part of the negative electrode (cathode) is luminous. At the point F this whole electrode produces light. If the voltage is increased from F to G, the region of the *abnormal glow discharge* is traversed; the cathode gets overheated under ionic bombardment (owing to ion-collisions, there is also ejection of the metal forming the cathode; this is the phenomenon of *cathodic sputtering* which will be used in Chap. VIII).

In all the region $CDEFG$, the discharge is maintained spontaneously; for which reason it is called the *self-maintained glow discharge.*

(e) When the point G is reached, the cathode emits electrons by thermionic effect.† Then the current increases greatly, and may reach several tens of amperes per cm^2. The tube resistance becomes very small and negative again. This has been used lately in arc radio oscillators.

This region is known, in fact, as the *arc discharge.*

3.13. BREAKDOWN VOLTAGE. PASCHEN'S LAW

The value of the breakdown voltage V_0 depends on the nature of the gas, on the pressure, and on the distance between the electrodes.

The Paschen Law states that, for all gases, the value of breakdown voltage depends on the product $p \times d$ of the pressure by the distance between the electrodes, and not on these factors taken separately.

It is to be observed that, if we draw the curve $V_0 = f(p \times d)$ of the the breakdown potential in terms of the product of the pressure and the distance between the electrodes, this curve shows a minimum (Fig. 3.9). This fact may be explained in the following way. It is known that the mean free path in a gas is inversely proportional to the pressure. The curve $V_0 = f(d/L)$ has then the same shape as the curve $V_0 = f(p \times d)$. If d is high in comparison to L (which occurs

† See Vol. II, Chap. III.

for high pressures or for great distances), the number of collisions between the particles is so high that ions and electrons can hardly reach an energy high enough to produce a high ionization, between two collisions.

Inversely, if d is small in comparison to L (low pressures or small distances), there are few molecules, and consequently few collisions.

In both cases, the breakdown discharge occurs only with high vol-

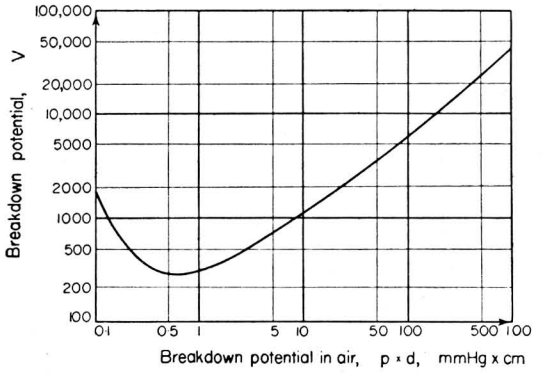


FIG. 3.9

tages, and hence the existence of a minimum which is experimentally found to happen when d is of the order of about 100 L.

Applications

From the above, it follows that:

(a) In a gas-tube, if it is required to obtain a minimum breakdown potential, it is necessary to choose the best value of the product $p \times d$.

(b) On the contrary, in a vacuum-tube, the breakdown potential may be very high.

Thus, gases at high pressure are often used to avoid breakdowns in devices using high voltages (electrostatic generators, high-voltage cables, etc.).

Inversely, electronic devices used aboard planes must be designed so as to avoid breakdowns due to the pressure decrease.

3.14. A VISUAL ASPECT OF THE GLOW DISCHARGE

The aspect of the glow discharge varies very much with pressure, from the thread-shaped luminous streak corresponding to pressures of

several cm Hg, to the low blue fluorescence of the glass happening around 10^{-2} mm Hg. In Chapter VI (manometers) it will be seen that this change of appearance allows an experienced observer to appreciate the pressure in a glass tube.

However, there is one characteristic aspect of the discharge: it is that corresponding to the most intense light emission and happens

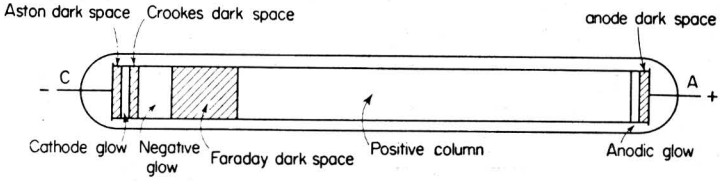


FIG. 3.10

around a pressure of the order of 1 mm Hg; the discharge then fills the whole section of the tube (this is the case for electric sign tubes) (Fig. 3.10).

(a) Very close to the cathode, there is a dark region, known as the *Aston dark space.*

(b) Just adjacent, there is a thin luminous layer, which is called the *cathode glow.*

(c) Then comes a new narrow region, slightly emitting, known as the *Crookes dark space.*

(d) Then follows a broader and bright region, called the *negative glow.*

(e) It is followed by a dark zone of about the same size, which is known as the *Faraday dark space.*

(f) The following bright region, called the *positive column*, emits 90% of the total light and fills the greatest part of the tube. This is what is seen in electric sign luminescent tubes. Its colour is characteristic of the gas: e.g. pink for air, orange for neon, blue-green for mercury vapour, etc.

(g) It is terminated by a brighter layer near to the anode and named *anodic glow.*

(h) Finally, the anode itself is covered with a dark layer known as the *anodic dark space.*

To what are these alternations of bright and dark areas due ? They probably occur because the electrons expelled from the cathode by the ionic bomdardment have firstly too low a speed to ionize the gas

(Aston dark space). Then with the energy increasing at the same time as the velocity, ionizing collisions occur with the molecules (cathode

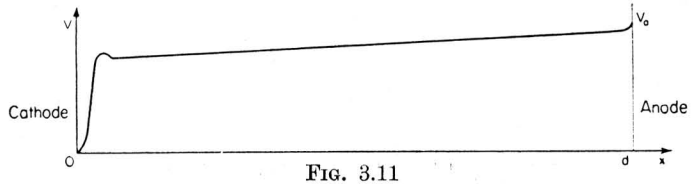


FIG. 3.11

glow). Electrons have then lost the greatest part of their speed, and the following area is slightly luminous, etc.

How is the potential distributed along the discharge ?

The greatest part of the potential drop occurs in the neighbourhood of the cathode, in the Aston dark space and in the cathode glow (Fig. 3.11). Further, and particularly in the positive column, the potential increases slowly. A small and sudden jump occurs in the anodic dark

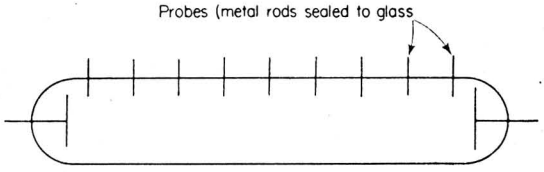


FIG. 3.12

space. These measurements have been done by inserting probes (metallic rods) in the tubes which allow measurement of the plasma potential by a method of balancing (in order to avoid a change in the potential distribution) (Fig. 3.12).

CHAPTER IV

PHYSICAL AND CHEMICAL PHENOMENA AT LOW PRESSURES

THE intrinsic nature of physical and chemical phenomena is not widely different, at low pressures, from that at atmospheric pressure. However, the following points may be mentioned:

(a) The speed of physical and chemical reactions may be greatly influenced by the decrease of the pressure.

(b) At low pressures, these reactions are generally more complete.

(c) Owing to oxygen and nitrogen rarefaction, these phenomena are purer, and the temperature may be increased without bringing about any parasitic phenomena.

The different physico-chemical reactions we will have to deal with in vacuum technique will be classified, following Prof. Boutry,† into three main kinds:

(a) Purely physical phenomena, relative to *changes of state* of a given substance: evaporation, sublimation, condensation, etc.

(b) *Chemical reactions* for which the pressure decrease, eventually accompanied by a change of temperature, has a great effect on combination and dissociation speeds.

(c) *Fixation of gases by solids*, phenomena including adsorption, chemisorption and solid solution.

Scarcely ever are these different phenomena not mixed in a more or less complex manner. In the course of the applications, some processes will be seen where two or three of them occur simultaneously.

† G. A. Boutry, 15th lesson (1).

4.1. PHYSICAL PHENOMENA RELATING TO CHANGES OF STATE

4.1.1. General remarks

4.1.1.1. *Definitions*

It is recalled that a substance may exist under three states: solid, liquid or gas. The transition from one to the other occurs under the combined action of temperature and pressure, and has the following names:

solid	liquid:	melting
	gas:	sublimation or evaporation.
liquid	gas:	evaporation or vaporization
	solid:	solidification.
gas	liquid:	liquefaction or condensation
	solid:	condensation.

4.1.1.2. *The Phase Diagram*

This name is given to the group of curves (Fig. 4.1) illustrating the physical changes of a substance, in terms of pressure and temperature, viz.:

(a) The curve plotting the pressure of saturated vapour against temperature (curve AIC).†

(b) The curve plotting the melting temperature against pressure (straight-line IB).

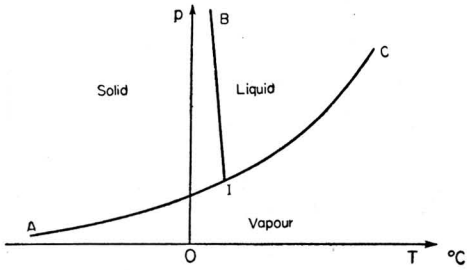


FIG. 4.1

The first curve is upper-limited at the point C, known as the *critical point*. Further, both curves intersect at the point I, the so-called *triple point*.

These two curves define the three possible states (phases) which the form of a body may take: if the characteristic point defining pressure and temperature is located in the area included between AI and IB,

† This curve often offers an angular point at I.

the substance is in the solid state; between IB and IC, the substance is in the liquid state; finally below the curve AIC, the substance is in the gaseous state.

The following peculiarities of the phase-diagram are recalled:

1. Suitably choosing the conditions of temperature and pressure, only one of the phases forms a stable equilibrium.

2. Taking convenient values of T and p, two of the phases may indefinitely coexist: this happens when the characteristic point is upon one of the curves.

In particular, when a substance is set in a closed space, it evaporates till the vapour pressure reaches the value defined by the curve AIC, at the temperature of the substance.

3. At the triple point I, there is indefinitely coexistence of the three phases in equilibrium.

4. At a temperature higher than that corresponding to the critical point C, it is impossible, whatever may be the pressure, to maintain the liquid phase: the substance passes wholly into the vapour state.

5. The values of temperature and pressure being conveniently chosen, a solid body may be sublimated, or its vapour may be condensed, without passing through the liquid phase (very important case in vacuum technique).

4.1.2. **Evaporation or sublimation in vacuum**

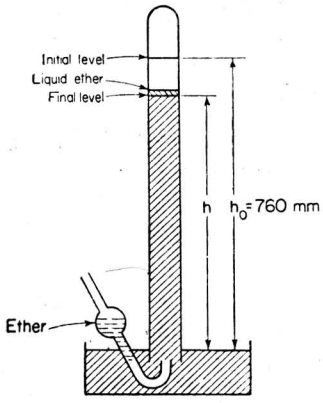


FIG. 4.2

Experiment. Introduce a volatile liquid (for instance ether) with the help of a bent pipette, into a barometric tube upturned on a mercury vat (Fig. 4.2).

The first drops entering the upper space are evaporated, and the mercury level is seen to decrease, thus showing a pressure rise. A certain quantity of ether may be introduced without a layer of liquid ether forming above the mercury. But if enough is added, the liquid begins to appear, and from then the mercury level does not move down; the liquid is said to be in equilibrium with its *satu-*

rated vapour (before the liquid appears, one has to deal with *dry vapour*). At this stage, there are as many molecules evaporating from the liquid to the vapour as molecules condensing from the vapour to the liquid.

4.1.2.1. *Heat of Evaporation or Sublimation*

To evaporate or sublime a substance, it must be provided with a certain quantity of heat.

The quantity of heat to be supplied to 1 g of a substance at the temperature T to change it into saturated vapour, is known as its *evaporation* or *sublimation heat* at the temperature T.

Let us calculate this evaporation heat. A body is heated in a closed and air-free vessel. A release of vapour occurs, so that to any temperature increase $\mathrm{d}T$, there corresponds a pressure increase $\mathrm{d}p$. At the temperature T, the pressure reached is $T\,\mathrm{d}p/\mathrm{d}T$. In these conditions, if V is the volume filled by 1 g of vapour,† the work to be supplied to produce this vapour is:

$$W = p\,\mathrm{d}v = V\,T\,\frac{\mathrm{d}p}{\mathrm{d}T}\,. \tag{4.1}$$

The corresponding quantity of heat, or heat of evaporation, is then:

$$\mathfrak{L} = \frac{V\,T}{J}\,\frac{\mathrm{d}p}{\mathrm{d}T} \tag{4.2}$$

(J is the mechanical equivalent of the calorie in the system used. 1 cal = 4·18 joules).

This is the *Clapeyron Formula*.

Experimentally, at high temperatures, it can be ascertained that the heat of evaporation may be expressed in the simple form:

$$\mathfrak{L} = \mathfrak{L}_0 - A\,T \tag{4.3}$$

($\mathfrak{L}_0$ = heat of evaporation at 0°C).

For example, Regnault worked out the following expression for water below 200°C:

$$\mathfrak{L} = 796 - 0{\cdot}695\,T \tag{4.4}$$

($\mathfrak{L}$ in calories, T in °K).

† The volume of the liquid or solid phase is neglected with respect to the gaseous phase. Besides, the reader's attention is drawn to the rudimentary character of this argument, the only quality of which is simplicity.

Consequently $\mathfrak{L}$ decreases when T increases. It of course vanishes at the critical point, as there only the vapour can exist.

4.1.2.2. *Calculation of Vapour Pressure*

The starting-point is the Clapeyron equation. At high temperatures, it will be assumed that:

(a) the vapour may be approximated to an ideal gas, so that:

$$p\,V = RT/M \tag{4.5}$$

(V is the volume filled by 1 g of vapour and M the molecular mass).

(b) $\mathfrak{L}$ varies linearly with T, according to eq. (4.3).

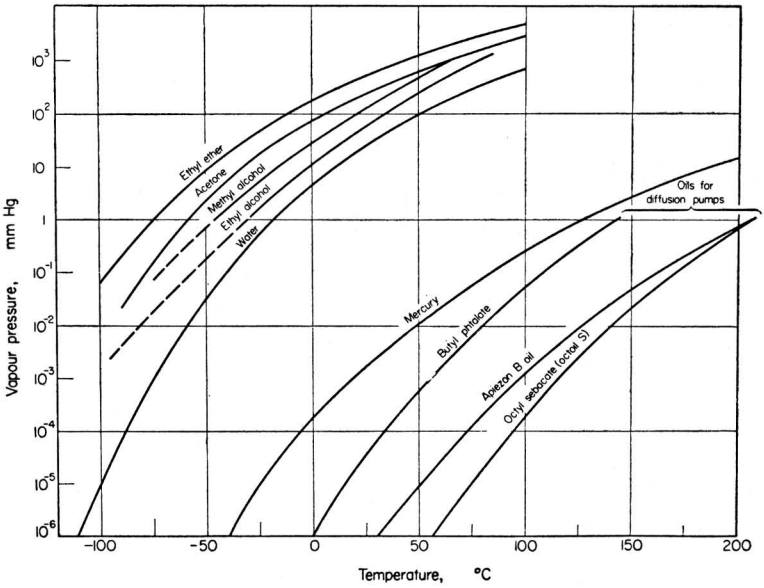


FIG. 4.3

Then, replacing V by $RT/p\,M$ and comparing eqs. (4.2) and (4.3), it may be written:

$$\mathfrak{L}_0 - A\,T = \frac{R}{J\,M}\,\frac{T^2}{p}\,\frac{\mathrm{d}p}{\mathrm{d}T}\,. \tag{4.6}$$

Separating the variables and integrating, this becomes:

$$\log p_0 = \alpha - \beta \log T - \frac{\mathfrak{L}_0}{T} \tag{4.7}$$

(α, β and $\mathfrak{L}_0$ are characteristic constants of the substance).

This expression gives the pressure p_0 of the saturated vapour in terms of its temperature. In an even more limited range of temperature, this equation may be simplified into:

$$\boxed{\log p_0 = \alpha - \frac{\mathfrak{L}_0}{T}} \quad . \tag{4.8}$$

Experience confirms this calculation well enough, for liquids and for solids.

The above equation is that of the curve AIC of the phase diagram (Fig. 4.1).

The constants α, β and $\mathfrak{L}_0$ have been measured for many substances, which allows one to calculate their vapour pressure p_0 at any temperature. Thus, Langmuir found for tungsten:

$$\log p_0 = 12{\cdot}24 - \frac{40{\cdot}26 \times 10^3}{T} \tag{4.9}$$

(taking p_0 in 10^{-3} mm Hg and T in °K).

Table 4.1 and the curves of Fig. 4.3 give the vapour pressure of some materials generally used in vacuum technique.

4.1.2.3. *Speed of evaporation or of sublimation*

In order to induce a molecule to leave the solid or the liquid from where it originates, it must be supplied with energy. In fact, there are powerful attraction forces between the molecules. But because of thermal agitation, these molecules are vibrating with oscillatory movements, zero at the absolute zero, but which increase in amplitude as the temperature rises. A moment comes at which the amplitude is so high that certain molecules may escape the attraction of neighbouring molecules and evaporate.

But we know that if a substance remains in the presence of its vapour, an equilibrium takes place when the saturated vapour pressure is reached.

In fact, the molecules comprising the vapour have also a thermal agitation, and some of them impinge on the substance, where they are recondensed. A balance occurs when the number of molecules recondensing is equal to the number of molecules evaporating.

On the other hand, if a vacuum is provided above a heated substance, there is no longer equilibrium, as the vapour is removed as soon as it is produced.

TABLE 4.1

Vapour pressure, boiling and melting point temperatures of various materials (temperatures in °C, for which the vapour pressure reaches the indicated values)

1 — ELEMENTS

Elements	Vapour pressure (mm Hg)									Melting point temperature (°C)
	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10	100	760	
Aluminium	724	808	889	996	1123	1280	1487	1749	2056	**660**
Antimony	466	525	595	678	779	895	1033	1223	1440	**630·5**
Arsenic						372	437	518	610	814
Barium	418	476	546	629	730	860	1049	1300	1638	850
Beryllium	942	1029	1130	1246	1395	1582	1770	2060	2970	1284
Bismuth	474	536	609	698	802	950	1130	1270	1420	271
Boron	1052	1140	1239	1355	1489	1648			*2550*	*2300*
Cadmium	148	180	220	264	321	394	484	611	765	321
Caesium	50	79	115	158	211	280	375	509	690	29
Calcium	408	463	528	605	700	817	983	1207	1487	810
Carbon	2129	2288	2471	2681	2926	*3300*	*3800*	*4300*	*4800*	3550
Cerium	1004	1091	1190	1305	1439	1599			2400	640
Chromium	907	992	1090	1205	1342	1504	1845	2139	2482	1900
Cobalt	1249	1362	1494	1649	1833	2056			2900	1478
Copper	946	1035	1141	1273	1432	1628	1879	2207	2595	**1083**
Germanium	897	996	1112	1251	1421	1635			2700	959
Gold	1083	1190	1316	1465	1646	1867	2154	2521	2966	**1063**
Indium	667	746	840	952	1088	1260	1452	1735	2080	157
Iodine						39·7	73·2	116·5	183	113
Iridium	1993	2154	2340	2556	2811	3188			4350	2454

Iron	1094	1195	1310	1447	1602	1783	2039	2360	2735	1535
Lead	483	548	625	718	832	975	1162	1421	1744	**327·4**
Lithium	325	377	439	514	607	723	881	1097	1372	186
Magnesium	287	331	383	443	515	605	743	909	1107	651
Manganese	717	791	878	980	1103	1251	1500	1792	2151	1260
Mercury	—23·9	—5·5	18	48	82	126	184	262	357	—38·9
Molyb-denum	1923	2095	2295	2533	2800	3102	3535	4109	4804	2622
Nickel	1157	1257	1371	1510	1679	*1870*	*2090*	*2350*	*2800*	**1452**
Palladium	1156	1271	1405	1566	1759	2000	*2300*	*2700*	*3200*	1553
Phosphorus (white)						76·6	128	197·3	280	44
Platinum	1606	1774	1904	2090	2313	2730	3146	3714	4407	**1773·5**
Potassium	91	123	161	207	265	338	443	586	774	63·6
Rhodium	1681	1815	1971	2149	2358	2607			3877	1967
Rubidium	60	89	123	165	217	283	389	514	679	38·5
Selenium						356	442	554	688	220
Silicon	1024	1116	1223	1343	1485	1670	1888	*2200*	*2600*	1420
Silver	767	848	936	1047	1184	1353	1575	1865	2212	960·5
Sodium	158	195	238	291	356	437	549	701	892	97·5
Strontium	361	413	475	549	639	750	898	1111	1384	770
Sulphur						184	244	327	444·6	113
Tantalum	2407	2599	2820	3060					*4200*	3000
Thorium	1686	1831	1999	2196	2431	2715			*4000*	1820
Tin	*823*	*922*	*1042*	*1180*	1320	1492	1703	1968	2270	**232**
Titanium	1134	1249	1384	1546	1742	1965			*3100*	1730
Tungsten	2554	2767	3016	3309	3640	3990	4507	5168	5930	3370
Uranium	1461	1585	1730	1898	2098	2338	*2700*	*3100*	*3500*	1133
Zinc	211	248	292	343	405	487	593	736	907	**419·5**
Zirconium	1527	1660	1816	2001	2212	2459			*3600*	1900

NOTES — (a) Melting temperatures indicated in heavy numbers can be used as standards.
(b) Temperatures indicated in italics have been obtained by extrapolation, or are given without any guarantee.

Compounds	Vapour pressure (mm Hg)									Melting temperature (°C)
	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10	100	760	
LiCl					670	783	932	1129	1382	614
NaCl	479	532	592	662	745	865	1017	1220	1465	800
KCl	457	508	567	635	710	821	968	1164	1407	776
$MgCl_2$						778	930	1142	1418	712
LiF	*590*	*650*	*730*	*804*	*935*	1047	1211	1425	1681	870
NaF	*620*	*690*	*760*	*840*	*950*	1077	1240	1455	1704	992
KF		*540*	*610*	*680*	*770*	885	1039	1245	1502	857
MgF_2	*900*	*980*	*1060*	*1180*	*1290*	*1450*	1655	1940	*2150*	1263
CaF_2	*980*	*1060*	*1180*	*1290*		1630	1865	*2170*	*2430*	1418
BaF_2							1655	1940		1350
MgO										2800
CaO	1583	1717	1873	2055	2271					
SrO	1420	1530	1631	1757	1901	2068	2262			2430
BaO	1150	1260	1395	1552	1742	*1950*	*2230*			1923
NiO	1248	1349								
PbO					*830*	943	1085	1265	1472	890
SiO_2					*1680*	*1830*	*2080*			1710
ThO_2	*1950*									3050
Al_2O_3						2148	2385	2665	2977	2020
PbS						852	975	1108	1281	1114
H_2O	−100	−88	−74	− 58	−39	−17·3	+11·3	51·6	100	0

Note — Temperatures indicated in italic numbers have been obtained by extrapolation, or are given without any guarantee.

Let us calculate the evaporation or the sublimation speed of a substance in vacuum.

For that, we shall consider again the case of a substance in equilibrium with its vapour. As is known, the number n_t of vapour molecules colliding with the walls and also with the surface of the substance, per sec and per cm^2, is:

$$n_t = \frac{1}{4} n v_m. \tag{2.54}$$

The total mass of these molecules is:

$$\mu = \frac{1}{4} n m v_m. \tag{2.56}$$

As there is a balance, this represents also the mass of the substance which evaporates per sec and per cm^2.

Now, if we exhaust the container, the equilibrium is upset: vapour condensation is suppressed, but evaporation does not change at all.

Then, the above expression gives *the speed of evaporation of a substance in vacuum*, that is, replacing n and v_m:

$$\boxed{\mu = p_0 \sqrt{\left(\frac{M}{2\pi R T}\right)}} . \tag{4.10}$$

This formula enables us to calculate the mass evaporated per sec, when the temperature T and the corresponding vapour pressure p_0 are known.

If a high vacuum is not obtained, and if a residual pressure p_1 of the vapour of this substance remains above it, the evaporation slows down and becomes:

$$\mu = (p_0 - p_1) \sqrt{\left(\frac{M}{2\pi R T}\right)} . \tag{4.11}$$

Finally, if evaporation occurs in the presence of a gas different from the vapour, with a pressure p, experience shows that the evaporation speed is greatly decreased: this is due to the fact that when gas molecules are present, they slow down the diffusion of vapour molecules.

4.1.2.4. *Summary of the Laws which Vapour Pressure Obeys*

(a) At a given temperature, the vapour pressure varies greatly from one substance to another; the most volatile substances (water, alcohol, ether) have the highest vapour pressures.

It is to be pointed out that solid substances usually have a very much lower vapour pressure than liquid ones. Nevertheless, it may be troublesome to obtain very good vacua (rubbers, waxes, etc.).

(b) At a given temperature, the vapour pressure is the same, the evaporation being effected in vacuum or in any gas (in this latter case, only the evaporation speed is decreased).

(c) At a given temperature, the vapour pressure is independent of the relative quantities of liquid or vapour in contact.

(d) For a given substance, the vapour pressure increases nearly exponentially with temperature.

4.1.3. Condensation. Principle of the cold wall

Let us achieve a certain vapour pressure in a vessel by heating it, as well as the product which it contains, to a certain temperature T_1 (Fig. 4.4).

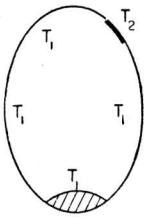


FIG. 4.4

Now, if a small part of the wall of the vessel is cooled down to a temperature $T_2 < T_1$, in the whole vessel the vapour pressure is found to be no longer p_1, but p_2 corresponding to T_2.† Furthermore, if this cooling down is strong enough, the vapour condenses on the part of the wall which is cooled (distillation). This results from the fact that vapour molecules reaching the wall at this place, lose their energy there and cannot rebound, as generally occurs when the wall is at the same temperature as the vapour.

4.1.4. Applications of evaporation and condensation phenomena to vacuum technique

(a) *Coating of thin solid layers by evaporation.*

This technique will form the subject of a special study in Chap. VIII.

(b) *Distillation under vacuum.*

† This supposes a broad communication to exist between the different parts of the vessel; that would be no longer so true if we had to deal with two vessels communicating by a small-diameter pipe.

This technique also will be studied in Chap. VIII.

(c) *Diffusion pumps* (see Chap. V, Sec. 5.1.3.3.ii.)

(d) *Limitation of vacuum by the vapour pressure of the fluids employed.*

It is readily understood that if a vacuum is achieved in a vessel or in a pipe containing liquids with a high vapour pressure, as long as these liquids are not completely evaporated, it will be impossible to obtain a pressure lower than the vapour pressure of the liquid, at the temperature it has reached. For example, if this liquid is water, it will not be possible to get the pressure lower than 17 mm Hg at 20°C. With mercury, it will not be possible to get less than 10^{-3} mm Hg, still at 20°C.

In addition we shall see that pumps use oil or mercury, for lubrication or for gas carrying: the same reservation must be applied to the lowest pressure that these pumps may produce.

This is the reason why, when very good vacua are required, the vessel to be exhausted is carefully baked during pumping; thus the evaporation of the liquids it may contain is accelerated (water condensed on the walls, especially); that is always done for electron-tube exhausting.

On the other hand, when it is required to prevent the vapour of the fluid used in the pump from passing into the vessel to be exhausted, a *cold trap* is inserted between this latter and the pump; this trap is made of baffles strongly cooled by liquid air or dry ice. (See Sec. 7.3.3.) So also can be condensed any noxious vapours.

(e) *Mercury-vapour thyratrons*

These gas-filled tubes use an atmosphere of mercury vapour produced by some drops of this metal which settle by gravity on the lower part of the bulb, and which is also the coolest one: it is verifiable that the vapour pressure is that which corresponds to the temperature of this region (see Vol. II, Chap. XI).

(f) *Getters*

We will see in Chap. V (Sec. 5.2) that in sealed bulbs, vacuum is maintained with getters; these are absorbent metals generally evaporated and then condensed on the bulb.

(g) *Electron-tube exhausting*

During the exhausting of tubes, it may be of interest to cool down the bulb (with an air-jet), whilst the electrodes are heated by induction

(see Sec. 8.4.2.2), or whilst the getter is evaporated (see Vol. II, Sec. 14.3). Thus, the metallic vapours are condensed in the cooled area, which avoids troublesome conducting coatings being formed in other parts (spacers, etc.).

(h) *Incandescent filament lamps*

An atmosphere of argon at a pressure of about 1 mm Hg is introduced in the bulbs of incandescent lamps; it causes the decrease of the filament evaporation and the increase of the life of the lamps.

4.2. CHEMICAL PHENOMENA AT LOW PRESSURES

4.2.1. **Review of some definitions**

(a) A chemical reaction is called an *exothermic reaction* when it evolves heat.

EXAMPLE: Formation of water from H_2 and $1/2\ O_2$.

(b) A chemical reaction is called an *endothermic reaction* when it absorbs heat.

EXAMPLE: Formation of acetylene (C_2H_2) from $2\,C$ and H_2.

(c) A chemical system is said to be in *equilibrium* if no reaction takes place in it.

The equilibrium is *stable* if a small change in the initial conditions involves only a small change to the system.

The equilibrium is *unstable* if a small change in the initial conditions involves important changes to the system.

4.2.2. **Law of the displacement of stable equilibrium**

Consider a chemical system in stable equilibrium. If the initial conditions of temperature or pressure are changed, and if that produces a chemical reaction, this reaction has an effect which runs counter to the modification (Law stated by Le Chatelier).

FIRST CONSEQUENCE. Influence of a change in temperature:

An increase of the temperature produces a chemical reaction, which should be an endothermic reaction if spontaneously brought about. Conversely, a decrease of the temperature produces a reaction which should be exothermic if spontaneously brought about.

EXAMPLE: When calcium carbonate is heated, it tends to decompose into carbon dioxide and lime:

$$CaCO_3 \rightleftarrows CO_2 + CaO.$$

If temperature is increased, $CaCO_3$ is dissociated.

If temperature is decreased, $CaCO_3$ is recombined.

SECOND CONSEQUENCE. Influence of a change in pressure:

If a reaction includes a gaseous phase, a pressure reduction tends to move the reaction in the direction of the gaseous phase; a pressure increase moves the reaction to the opposite direction.

EXAMPLE: Calcium carbonate placed in vacuum will tend to decompose, and conversely,

$$\underset{\text{solid phase}}{CO_3Ca} \rightleftarrows \underset{\text{gaseous phase}}{CO_2} + CaO$$

4.2.3. Applications to electron tubes

(a) *Dissociation of alkali-earth nitrides*†

From 1925 to 1940, tens of millions of radio tubes were manufactured by the following process: a tungsten filament previously copper-plated and oxidized, is plunged into an aqueous solution of barium nitride BaN_6, a salt of the hydrazoic acid HN_3 (these materials are dangerous explosives). During the pumping, the electron tube is heated to about 400°C. There is obtained:

$$BaN_6 \rightarrow Ba + 6\,N \text{ (absorbed by the pump)}.$$

Then, barium is left on the filament. After the pumping, heating of the filament enables the barium to reduce the copper oxide. Finally, we obtain tungsten covered with copper and barium oxide (see the working of complex cathodes in Vol. II, Sec. 4.3).

(b) *Dissociation of alkali-earth carbonates*

Modern receiving radio tubes are provided with a nickel cathode covered with a layer made of a mixture of barium and strontium carbonates. The aim is to obtain oxides. The cathode is then heated at about 1100°C while the tube is pumped:

$$BaCO_3 \rightarrow BaO + CO_2 \text{ (absorbed by the pump)}.$$

If CO_2 were not exhausted as soon as it is formed, the reaction, being reversible, would not be complete. (Oxide-coated cathodes will be studied in Vol. II, Sec. 4.3).

(c) *Cycle for tungsten heated in the presence of water vapour*‡

In a radio tube or in an electric lamp provided with a tungsten filament, if traces of water vapour remain, this is enough to cause a

† G. A. Boutry, 17th lesson (1).

‡ S. Dushman, p. 679 (3).

quick destruction of the filament. In fact, at about 2600°K, water vapour reacts upon tungsten:

$$W + 2\,H_2O \rightarrow WO_2 + 2\,H_2.$$

But at this same temperature, WO_2 is more volatile than tungsten and consequently it will be evaporated and driven towards the walls of the bulb. On the way, it meets with hydrogen molecules previously formed, and, the temperature being lower, it recombines with them to restore tungsten, which deposits on the bulb, and to give water vapour which starts the cycle again. The rupture of the filament occurs, in these conditions, much more quickly than by simple evaporation of the tungsten in vacuum.

4.3. PHENOMENA OF FIXATION OF GASES BY SOLIDS

Experience shows that solid materials may fix large quantities of gas. These phenomena may be divided into three kinds:

(a) Physical adsorption.

(b) Chemical adsorption or chemisorption.

(c) Absorption of gases by metals, in which, to the above two phenomena a third one is joined, viz. the solution of gases in metals.

These different phenomena are rarely encountered in the pure state, but in order to simplify, they will be studied separately.

Finally, a few words will be said about the absorption of gases in an electric discharge.

4.3.1. **Physical adsorption**

This is the name given to the adhesion of gas in very thin layers to the surface of solid materials.

First Experiment. Let us cleave a mica sheet. Then, if the two parts are immediately applied one against the other, they stick. They cease to do this after a few minutes of exposure to air, owing to the fact they have been covered by adsorption with nitrogen and oxygen molecules.

Second Experiment. Some glass is ground in a mortar and to it is added water made free from air by boiling, in order to obtain a clear mixture, without any visible bubble of gas. The mixture is poured

into a long-necked flask which is only filled up to two-thirds. Then, if the flask is pumped, the volume of the liquid increases, and the liquid enters the neck. If air is allowed to fill the flask, again the liquid returns to its original volume with a rough shock. If a vacuum is kept on, some bubbles tend to escape.

These facts are explained by assuming that every grain of glass is coated with a thin layer of air.

4.3.1.1. *Principal Laws of Physical Adsorption*

(a) *Adsorption is a surface phenomenon*: the mass of gas adsorbed is proportional to the surface area and not to the volume of the solid. It must, however, be pointed out that the true adsorption surface may be much greater than the apparent surface, in the case of porous materials: for instance, it has been proved that charcoal has an active surface of 700 m^2 per g, and silica gel an active surface of 500 m^2 per g. It is, however, assumed that adsorbed layers are *monomolecular*.

(b) *Adsorbed gas molecules are fixed often by very strong forces*, known as *London–Van der Waals forces*; these forces are demonstrated to be proportional to $1/r^7$ (r = distance from the adsorbed molecule to the adsorbing one). From this it follows that the release of adsorbed molecules is very often difficult.

(c) *Adsorption is an exothermic phenomenon*, involving gaseous phase. It follows also that the law of the displacement of stable equilibrium may be applied to it, and it may be deduced that:

Adsorption increases with pressure;

Adsorption increases when temperature decreases.

This is perfectly confirmed by experience.

(d) *Adsorption is a reversible phenomenon*, that means, theoretically, that if a solid and a gas are brought together, at the same temperature and pressure conditions, there will arise identical adsorbed quantities of gas (the gas release is named *desorption*, commonly called *degassing*).

(e) For a given solid and in given conditions, *adsorption depends greatly on the nature of the gas.*

4.3.1.2. *Isotherms and Isobars of Adsorption*

Isotherms of adsorption are experimental curves giving the mass μ of a gas adsorbed per gramme of a solid, as a function of pressure and with temperature as a parameter.

Freundlich proposed expressing them by an empirical formula:

$$\mu = \alpha\, p^{1/n}\, e^{-Q/kT} \tag{4.12}$$

α, n and Q depending upon the substances in question.

This formula, in which $n = 2$ to 5, is rather well verified in the case of very porous adsorbing materials (charcoal, silica gel), as well as in the case of metals. As the tangent at the origin of the corresponding curves is vertical (Fig. 4.5), it is obvious that even for very low residual pressures, large quantities of gas remain. That explains why it is so difficult to expel the last traces of a gas fixed by adsorption on the above materials.

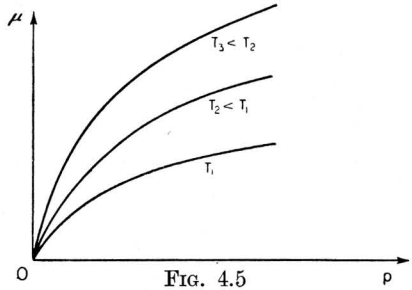


FIG. 4.5

Isobars of adsorption are experimental curves giving the quantity of adsorbed gas against temperature, with pressure as parameter (Fig. 4.6).

They are roughly decreasing exponential curves.

Consequently, to remove the adsorbed gases, it will be required, separately or even better simultaneously:

(a) to reduce pressure;

(b) to increase temperature.

The Freundlich equation does not mention the existence of a saturation of the adsorbing material.

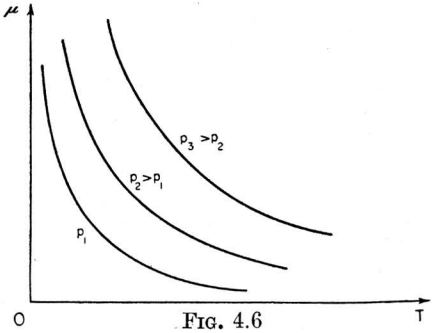


FIG. 4.6

Now, this saturation exists: Langmuir showed that as a maximum there can only be adsorbed a quantity of gas corresponding to a monomolecular layer.

Consequently, he proposed the following equation:

$$\mu = \frac{a\,p}{b\,p + 1} \tag{4.13}$$

giving a saturation $\mu \to a/b$ for $p \to \infty$.

This expression, the curve of which does not give a vertical tangent at the origin (and consequently which foreshadows an easy degassing) is quite well checked for adsorbing materials presenting a well determined surface, such as glass or mica, as well as for porous adsorbants in the case of high pressures (Fig 4.7).

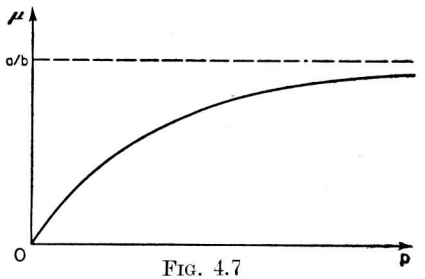


FIG. 4.7

4.3.1.3. *Examples of Physical Adsorption*

Adsorption of gases by glass†

The fixation of gases by glass occurs mainly by adsorption on the surface.‡ The following are some experimental facts:

(a) the fixed gases are mainly water vapour, then CO_2, and finally, in small quantities O_2, N_2, and CO.

(b) The total quantities of fixed gases depend upon the chemical composition of the glass.§

TABLE 4.2

Kind of glass	H_2O	CO_2	$N_2 + O_2 + CO$	Total Volume (mm^3/cm^2)
Lime-glass	88 to 93%	2 to 10%	about 1%	25 to 40
Crystal-glass	about 96%	1·5 to 2%	about 1·5%	< 20
Boro-silicate glasses	30 to 40%	40 to 45%	20 to 30%	< 1·5

It seems that on the one hand the total quantity of fixed gas, and on the other hand the quantity of fixed water vapour, are directly related to the amount of soda or potash contained in the glass.

Degassing of glass. Let us point out two interesting experiments of Langmuir: the first one dates from 1913:

† The other physical or chemical properties of glasses will be studied with more detail in Vol. II, Sec. 12.2.1.

‡ There are also small quantities of gas which are dissolved in the mass during the glass-making and the melting of its component materials.

§ The quoted numbers relate to samples of glass washed with sulpho-chromic acid, rinsed out with distilled water and dried under vacuum at 20°C. Then they are baked under vacuum around softening temperature (4 - 500°C according to the type), and the gases removed are collected.

1. Some bulbs with an inner surface of 200 cm^2 are carefully dried by putting them in vacuum for 24 hr. Then they are heated in vacuum successively at 200, 350 and 500°C, for periods of 3 hr at each temperature. Table 4.3 gives, for each temperature, the total quantities of gases of each kind evolved from the glass:

TABLE 4.3

	At 200°C	At 350°C	At 500°C
H_2O	200 mm^3	300 mm^3	450 mm^3
CO_2	5 mm^3	20 mm^3	30 mm^3
N_2	2 mm^3	4 mm^3	5 mm^3

At each temperature, gas is emitted only during half an hour, after which a new temperature rise is required to bring about a new emission.

The conclusions of this test deduced by Langmuir are the following:

(a) Even at 500°C, it is certain that all the gas adsorbed by the glass is not released.

(b) However, it is probable that when glass has been heated in vacuum at 500°C, it must emit at lower temperatures only very small quantities of gas.

2. However, in 1918, Langmuir pointed out the following facts: Some electric filament lamps using boro-silicate glass for the bulb, were divided into three lots. The first lot were baked during exhausting at 450°C; the second one, at 550°C; and the third one, firstly at 550°C, and then at 400°C.

The first lot had a mean life of 575 hr, the second one of 300 hr, and the third one of 900 hr.

Langmuir explains this phenomenon as follows: the heating at a temperature lower than 500°C eliminates only superficial gases. Therefore, in the depth there is a certain quantity of gas remaining which escapes slowly, thus reducing (in a long time) the life of the tube. When heating between 500 and 600°C, superficial gases are released, but they are replaced by gases coming from deep layers which are adsorbed on the surface, and from where they will evolve rather quickly during the working of the lamp.

Langmuir advises then the baking of glass bulbs, in several steps of decreasing temperatures (this is easily done by leaving the oven to cool slowly, after reaching a maximum near to the glass softening point).

Adsorption of gases by mica. Though mica has not formed the subject of so many tests as glass, it may be supposed that, because of the physical (very smooth surface) and chemical (mica is also a mixture of silicates) analogies of these two substances, the adsorption of gases by mica will be very similar to the adsorption by glass, qualitatively and quantitatively. However, the following differences will be pointed out:

(a) Because of its stratified structure, the actual surface of adsorption of mica is much larger than the glass one.

(b) Besides the water fixed by adsorption, mica contains "crystallization" water evolving around 900°C and bringing about the swelling and then the crumbling of the material.

The degassing and the normal use of this substance must be designed so as to prevent all or parts of the mica pieces exceeding a temperature of 600 or 700°C

Adsorption of gases by activated charcoal. Activated charcoal sometimes used in vacuum technique, is obtained by heating in air at 650°C the soft part of a coconut, till vapour emission stops. Then the temperature is increased to 900°C for a few minutes. Lastly, the product is heated in vacuum at 440°C for several hours.

Because of its porosity, the product so obtained is endowed with extraordinary properties of adsorption: its true surface is about 700 m^2/g.

It was used much more before the invention of diffusion pumps for producing good vacua.

Adsorption by charcoal obeys the Freundlich equation rather well (Sec. 4.3.1.2.), with $n = 1$ to 4 according to the gases. It results, therefore, that the quantity of adsorbed gas rises with pressure and increases exponentially when the temperature decreases: it is for this reason that the best results are obtained by cooling it to the temperature of liquid air: −180°C.

Table 4.4 gives the quantities of gas fixed by charcoal, and allows one to check this temperature influence. Besides, it will be seen that gases with the highest boiling-points are the highest (in the absolute scale) of the most easily adsorbed.†

† Moreover, it may be mentioned that some other porous materials can be used for gas fixation. Especially *chabasite* may be named (double natural calcium and aluminium silicate) which, at equal mass, fixes five times more gas than coconut-coal; silica gel, which is of convenient use but which fixes ten times less gas than charcoal.

TABLE 4.4

ADSORPTION OF GASES BY ACTIVATED CHARCOAL

Gas	Adsorbed volume in cm^3 per g at 760 mm Hg (S. T. P.)			Melting point of liquefied gas (°C)
	+15°C	−78°C	−180°C	
H_2O	700			+100
SO_2	380			− 10
NH_3	181			− 33
H_2S	99			− 62
C_2H_2	49			− 84
CO_2	48	160		− 78
CO	9	100	150	−190
O_2	8		225	−182
N_2	8	45	200	−195
H_2	5	10	100	−252
He	ε	1	2	−272

Materials fixing water vapour. Some applications of vacuum technique (for example drying) are made much easier by placing at one point of the vacuum system a material strongly adsorbing water vapour.

Table 4.5 allows us to estimate, in relative value, the adsorbing capacities of various materials: the numbers give the quantity of water vapour left in the vessel after the action of different chemical agents, the starting quantities being the same.

TABLE 4.5

Material	mg of water left per l. of gas after the effect of the material
Charcoal at −180°C	$1{\cdot}6\times10^{-22}$
Phosphorus pentoxide	2×10^{-5}
Caustic potash	2×10^{-3}
Silica gel	3×10^{-2}
Sulphuric acid (at high concentration)	3×10^{-1}
Anhydrous calcium chloride	$3{\cdot}6\times10^{-1}$

Other applications of physical adsorption.

(a) Getters (adsorbing substances put in a sealed bulb to improve the vacuum) work mostly by adsorption (see Chap. V).

(b) During pumping, electron tubes are carefully baked (heated at about 400 – 500°C) to remove gases, and especially the water vapour fixed on the bulb walls and on the surface of the electrodes (see Vol. II Sec. 14.3).

(c) If adsorption phenomena are very often a trouble owing to the difficulty of releasing the adsorbed substances, they are useful in some special cases. For instance, a material adsorbed on some surface gives a vapour pressure much lower than when it is in the solid state: then it does not evaporate so easily. Thus since at 700°C barium has a vapour pressure of 0·1 mm Hg, 1 cm^2 of bulk barium would allow 2 mg of metal to be evaporated per sec. Fortunately, it is observed that oxide-coated cathodes, which are mainly composed of barium atoms adsorbed on a convenient base, show a much smaller loss of weight (see Vol. II, Sec. 4.3.2).

(d) In industry, "bone-black" (bone-coal) is used to decolorize some products: the colorants are fixed by adsorption on the carbon.

(e) Gas-masks retain the poisonous gases by adsorption upon suitable substances.

(f) Chromatography allows the separation of mixed chemical products, by using the differences in their adsorption by porous substances, such as alumina.

4.3.2. **Chemisorption**

Of course, any chemical affinity between a gas and a solid will lead to a fixation of the first one by the second; this fixation brings about chemical connection forces different from Van der Waal's forces, and very often higher than these.

For example, Langmuir mentions that at 1500°C, over one year is required to remove an oxygen film formed on a tungsten filament. Besides, the fact that, at this same temperature, hydrogen has no action on the aforesaid film, proves indeed that the oxygen so fixed does not behave as when it is in the gaseous state.†

It must also be pointed out that when charcoal having adsorbed oxygen is degassed, a small amount of carbon monoxide is found in the extracted gas, even at low temperature.

Finally, it must be stated that nitrogen and hydrogen fixed by barium getters, are fixed partly in the form of nitrides or hydrides (see Chap. V, Sec. 5.2).

† C. J. Smithells, *Gases and Metals*, Chapman and Hall, London 1937.

It is to be noticed there is an important difference between the chemisorption process and adsorption: while this latter is the more efficient the lower the temperature, chemisorption does not occur at low temperatures, and on the contrary, quickly rises with temperature.

4.3.3. Absorption of gases by metals

4.3.3.1. *Definition*

To use an illustrative expression, metals are true "gas sponges". According to the circumstances, they may absorb from several times to several hundred times their own volume.

It is certain that this absorption happens with a simultaneous triple process:

(a) by physical adsorption;
(b) by chemisorption, for the gases chemically reacting upon the metal;
(c) by solution, i.e. by diffusion in depth of gaseous molecules, between metallic atoms.

It is the existence of this last phenomenon which distinguishes metals from the other adsorbing solids.

4.3.3.2. *Laws of Gas Absorption by Metals*

Existence of a saturation. Absorption of gases by metals, just like physical adsorption, shows a saturation with time (Fig. 4.8).

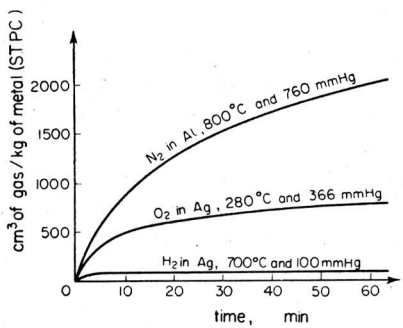


FIG. 4.8. Absorption of various gases by various metals. These curves show the existence of a saturation. (After Smithells)

The volume of gas fixed per unit-weight of metal, when this saturation is reached (this volume being measured at normal conditions of temperature and pressure), is named the *solubility.*

Time constant of absorption. Absorption of gases by metals requires a time much longer than physical adsorption: whilst the latter happens in a time of about 1 min, in the first the saturation requires a time between a few minutes and several hours when heated, or even several days in the cold state (Fig. 4.8).

This difference is explained by assuming that, whilst adsorption is a surface phenomenon, in the case of metals there is a diffusion of gases in depth between the metallic atoms.

Relation between absorption and pressure. Whatever may be the process of absorption, it is observed that, for gases other than inert gases, the gas solubility in a metal is always proportional to $\sqrt{p}$ and not to p: that is explained if gases are assumed to diffuse into metals not as diatomic molecules, but as distinct atoms.

In fact, let v be the volume of gas (assumed diatomic) to be absorbed. Every time a quantity of this gas (measured at a pressure p) is absorbed, the pressure, which should fall by a quantity $\mathrm{d}p$ if absorption were occurring in the molecular form, decreases, other things being equal, only by $\mathrm{d}p/2$ if absorption occurs in the atomic form (as each molecule is separated into two atoms).

It may be written that:

$$p\,\mathrm{d}v = v\,\frac{\mathrm{d}p}{2} \tag{4.14}$$

whence:

$$\log v = \frac{1}{2}\log p + \log k \tag{4.15}$$

and:

$$v = k\sqrt{p}. \tag{4.16}$$

Note that this formula could be more derived by using the law of (mass) action.

Relation between absorption and temperature. There is no absolute rule, as will be seen in the following section. Some gases are absorbed by certain metals in quantities rising exponentially with T; others in decreasing quantities; for others lastly, the curve $s = f(T)$ (solubility against temperature) shows one or several maxima and minima. This is due to the fact that absorption brings into action numerous processes (adsorption, chemisorption, etc.) on which temperature acts in different ways.

Relation between absorption and the nature of the gas and of the metal†.

(a) *Hydrogen.* This is mostly absorbed by chemisorption, forming hydrides with alkali-metals, with alkaline-earth metals, and also with Si, Ge, Sn, Pb, Sb, Bi.

It is absorbed in true solution in quantities exponentially increasing with T and proportionally to $\sqrt{p}$ according to the relation:

$$s = A\sqrt{(p)}\,\mathrm{e}^{-Q/kT} \tag{4.17}$$

in the following metals: Cu, Ag, Cr, Mo, W, Fe, Co, Ni, Al, Pt.

This relation presents important anomalies in certain cases. For instance, a remarkable phenomenon occurs during the absorption of

† For more details, see: S. Dushman, Chap. IX (3).

hydrogen by iron: a sudden and reversible rise of the absorbed quantity of hydrogen occurs around 900°C. A sudden pressure decrease results (Fig. 4.9). This phenomenon is used in "iron–hydrogen" regulators (see Vol. II, Sec. 11.7).†

Hydrogen is absorbed, still in true solution and proportionally to $\sqrt{p}$, but in decreasing quantities when T rises, in some metals such as Pd, Zr, Ta, Ti. The quantities of hydrogen dissolved by these metals are very large: at 20°C and 760 mm Hg, palladium dissolves 900 times, tantalum 750 times, zirconium 1500 times and titanium 1800 times its own volume of hydrogen (see Sec. 5.2.2, the use of the two last metals as "getters") (Fig. 4.10).

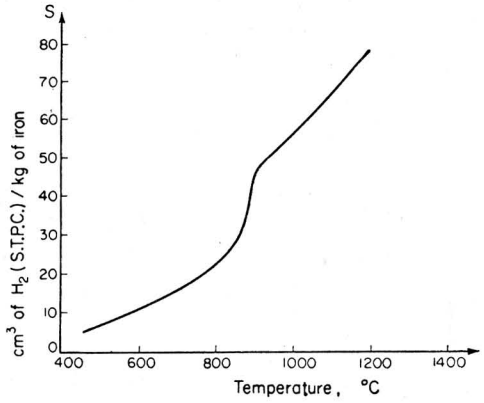


FIG. 4.9. Absorption of hydrogen by iron

Finally, hydrogen is not absorbed by Au, Zn, Cd.

(b) *Oxygen.* This is absorbed by chemisorption with formation of oxides in most metals, except the noble metals (Pt, Ir, Os, Pd, etc.). This absorption is peculiarly strong with the alkali, alkaline-earth and metals of the group IVb of the periodic table (Ti, Zr, Hf, Ce, Th).

In addition, it is absorbed by solution, and proportionally to $\sqrt{p}$ in some other metals, such as Ag, Cu, Co, Fe. In this case, the absorption passes, as a function of temperature, through a minimum, which occurs around 400°C in the case of silver and copper (Fig. 4.11).

With copper, oxygen forms in the mass, granules of oxide Cu_2O, which are reduced during further baking of the metal in hydrogen or under vacuum, so making the metal porous and brittle: thus the interest, in electron tube manufacture, of copper melted in vacuum [OFHC (oxygen-free-high-conductivity) copper].

The "pitting" of silver is also a well-known phenomenon: the solubility of oxygen in silver increases 40 times between 920 and 970°C.

† Similar phenomena (sudden increase in the solubility at an ascertained temperature) occur with nickel and copper; but in the case of these metals, this anomaly occurs in the vicinity of the melting-point.

The melting-point of silver being located at 960°C, melted silver dissolves large quantities of oxygen which, during the solidification, are suddenly released, bringing about the formation of gas-pockets in depth and on the surface.

(c) *Nitrogen.* This is only absorbed by chemisorption, i.e. by metals with which it forms nitrides. This is especially the case with Fe, Ta, Mo, W, Zr, Ti. The solubility is proportional to $\sqrt{p}$.

The curve of nitrogen solubility in iron offers even more anomalies than that of hydrogen in the same metal. Weak below 800°C, it increases by a factor 20 around 900°C, it remains nearly constant till about 1400°C, decreases by half in the range 1400–1600°C, and rises again very quickly in the molten iron (Fig. 4.12).

In molybdenum and tungsten, nitrogen dissolves in quantities increasing almost exponentially with temperature (Fig. 4.13).

(d) *Carbon monoxide.* According to Dushman, it behaves as does nitrogen, i.e. it is absorbed by chemisorption, producing carbon compounds: e.g. Fe and Ni.

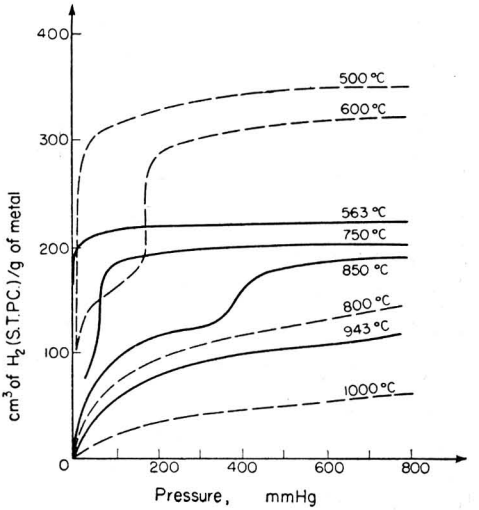


FIG. 4.10. Absorption isotherms of hydrogen by zirconium and titanium

——— zirconium
····· titanium

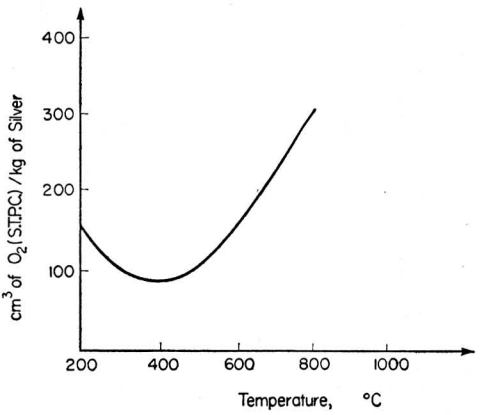


FIG. 4.11. Absorption of oxygen by silver at 760 mm Hg

4.3.3.3. *Diffusion of Gases through Metals*

The absorption of gas in metals being a phenomenon

occurring in depth, it is evident that after a greater or less time, depending on the nature of the metal and its thickness, and the nature and pressure of the gas, the latter will succeed in passing through the metal.

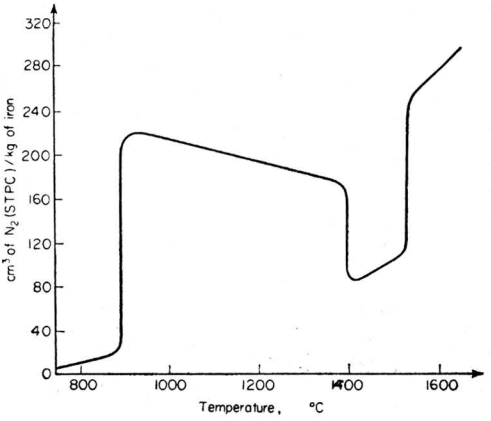


FIG. 4.12. Absorption of nitrogen by iron

The most remarkable example is the porosity of palladium for hydrogen; but in other cases, it is very often difficult to distinguish this phenomenon from a simple desorption of a metal not adequately degassed.

For instance, it is certain it occurs appreciably in the case of air and iron: it is known that the manufacture of electron tubes using iron bulbs gave rise to disappointments because of the wall porosity. This phenomenon is considerably reduced in the case of copper, for transmitting tubes have been constructed for thirty years, with a part of the envelope made of this metal.

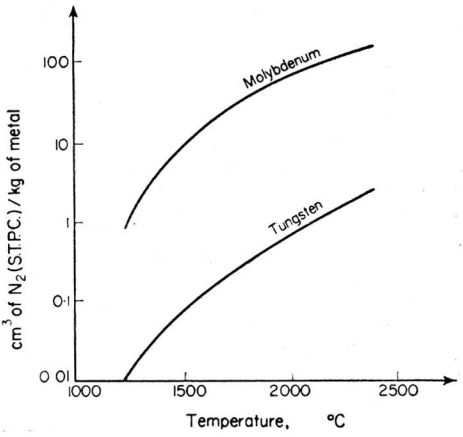


FIG. 4.13. Absorption of nitrogen by molybdenum and tungsten

According to Smithells, it is experimentally observed that the speed of diffusion of a gas through a metal, in unit-volume per unit-time corresponds rather well to the formula:

$$v = \frac{a}{d} \sqrt{(p)}\, e^{-b/T} \qquad (4.18)$$

in which a and b are constants depending on the metal and the gas, d is the thickness of the metal, p the pressure and T the absolute temperature.

Figure 4.14 gives the diffusion speeds for different metal–gas systems. Especially will it be noticed the ease with which palladium is traversed by hydrogen (at 130°C, it passes per minute 1 mm^3 of H_2 at 760 mm Hg through a wall of Pd 1 cm^2 of surface and a thickness of 1 mm).

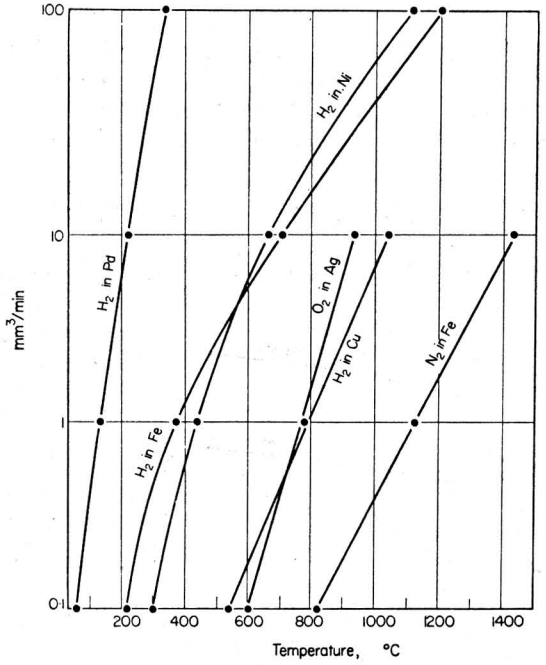


FIG. 4.14. Speeds of diffusion of various gases through various metals at 760 mm Hg. Metal thickness: 1 mm. Surface: 1 cm^2.

This property is used for leak-finding, as well as to control the introduction of H_2 into a vessel (see Chap. VIII).

4.3.3.4. *Desorption*† (release of gases contained in metals)

Empirically, desorption has been proved to obey the following laws:

Influence of pressure. The absorption of gases by metals was seen to vary as $\sqrt{p}$ and not as p. Consequently, desorption will follow a similar law, i.e. a fall of p will force the gases to come out of the metal.

† Degassing in technical slang.

However, this law in $\sqrt{p}$ is unfavourable concerning the case of desorption of the gas, because, as it has been seen in the case of adsorption by porous substances, the fact that the curve $s = f(p)$ presents, around $p = 0$, a vertical tangent, means that a notable quantity of gas remains in the metal even when p is very small.

Influence of temperature. Here, the phenomena are more complicated still. In fact, many metals absorb gases in quantities increasing with temperature, owing to chemisorption. It might be thought it is neither required nor favourable to heat metals in order to degas them.

But, nothing of the kind. Actually, if a temperature rise is combined with a pressure fall, the thermal agitation of metal atoms as well as of gas molecules, will have the objective of ejecting the latter, in order to balance the pressure in the metal with the outside pressure.

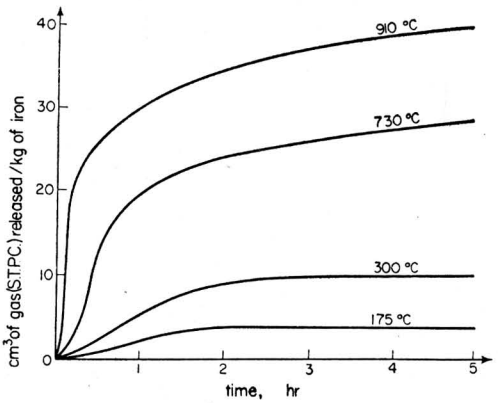


FIG. 4.15. Degassing of electrolytic iron. (After Hughes)

This is verified not only with metal-gas systems for which absorption is an inverse ratio of temperature (H_2—Pd, H_2—Ta, etc.) but also with those presenting the inverse relation (H_2—Ni, H_2—Fe, N_2—Fe, etc.).

Influence of the nature of gas and of metal. Oxygen is by far the most difficult gas to extract, especially out of easily oxidizable metals (for instance, iron).

On the contrary, hydrogen is very easy to release, even out of metals with which it forms hydrides, owing to its easy diffusion (connected with its low molecular mass), and the instability of hydrides at high temperature.

This is the reason why metals intended for electron tube construction are submitted to heating for 20 min at 900°C in this gas. Hydrogen reduces oxides and releases absorbed gases whose place it takes; during the pumping of the tube, absorbed hydrogen will easily be released (see Sec. 8.4).

Figures 4.15 and 4.16 give the shape of degassing curves obtained with some metal-gas systems.

These curves are seen to obey fairly well a law of the following form:

$$v = a\,(1 - e^{-bT}) \tag{4.10}$$

in which:

v is the volume of the evolved gas measured at S. T. P. conditions; t is the time; a and b are constants depending on the gas and the metal.

Quantity and nature of gases contained in various metals. Table 4.2 summarizes various results obtained from 1918 to 1944. The following conclusions can be deduced:

(a) Bessemer steel contains huge quantities of gas: more than 200 cm per cm^3 of metal, among which there are 8 cm^3 of O_2, a gas difficult to release.

(b) Special irons contain a lower total quantity of gas, but it is mostly composed of O_2.

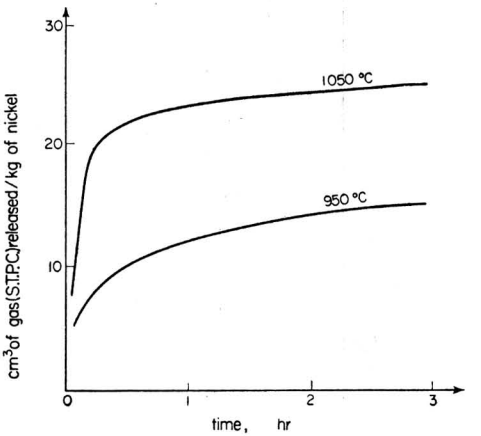


FIG. 4.16. Degassing of a nickel wire. (After Smithells)

(c) Common nickel contains rather a lot of gas (8 to 40 cm^3 per cm^3 of metal), but does not contain any oxygen at all, which explains why refining by electrolysis or melting in vacuum so easily allows the release of occluded gases.

(d) Refined copper (by melting in vacuum) contains a little gas and no oxygen at all.

(e) Tungsten and molybdenum are only very slightly contaminated by gases.

(f) Lastly, graphite is easily refined.

In conclusion, in electron tube manufacture, the use of iron will be avoided, except in some peculiar cases (see Vol. II, Sec. 12.1).

It is preferable to use, for conventional radio tubes, refined nickel or nickel alloys (copper-nickel, stainless steel... etc.).

TABLE 4.2

GASEOUS ANALYSIS OF VARIOUS METALS

Author	Metal	Name	Composition (%)	Total quantity of evolved gas (cm^3/kg)	Temperature reached (°C)	Gas composition in % of volume					
						O_2	H_2	N_2	CO	CO_2	SO_2
Hessenbruck 1929	Iron	Electrol.	C = 0·02 Si = 0·02 Mn = 0·02 S = 0·003	212·6	1550	33	53				
		Armco	C = 0·02 Mn = 0·05	540·4	1550	80	14·5	5·5			
		Swedish	C = 0·04	1220	1550	87	11	2			
Norton & Marshall 1944		New Iron(5)	C = 0·05 Si = 0·008 S = 0·006 P = 0·008 Mn = 0·18	70	1370						
Alleman & Darlington 1918	Steel	Bessemer	C = 0·1	28100		4	10·5	52	33	0·5	

Hessenbruck 1929		Cube(1)		4800	1470	3·5	4·2	90	2·3	
		Mond(2)		1130	1470	24·7		72·4	2·9	
		Electrol.		79	1470	79		21		
Norton & Marshall 1944	Nickel	Previously melted under vacuum		2·8	1090					
Hessenbruck 1929	Copper	Refined(3)	99·98% Cu	17	1250	14	6	20		60
		Electrolytic		80	1250	40		50		10
Norton & Marshall 1944	Molybdenum			0·8 to 8 (according to the sample)	1800	5(4)	60(4)	30(4)	5(4)	
Norton & Marshall 1944	Tungsten			0·3	2400	3	67	30		
Norton & Marshall 1944	Graphite	Not treated		270	2150					
		Treated under vacuum at 1800°C		1·5 to 12	2150					

(1) Nickel obtained by the classical process of oxide reduction by charcoal.
(2) Nickel obtained by carbonyl process.
(3) Averages of four samples from different sources.
(4) Averages of the commonest values.
(5) Iron made by "General Reduction Corporation" by melting in vacuum.

OFHC copper is also a first-class metal concerning the gas occluded. It is widely employed in microwave-tube manufacture (see Vol. II, Chap. 9), but precautions must be taken for limiting temperature rise, owing to its low melting-point and high vapour pressure.

Tungsten and molybdenum, because they have a high price, are only used for realizing parts working at very high temperature (heaters, anodes), and also for certain glass-to-metal seals (see Vol. II, Sec. 14.2).

Lastly, graphite will have some applications due to its high melting point and thermal emission coefficient (anodes).

4.3.4. **Absorption of gases by an electrical discharge**

It is a common fact of experience in electron tube manufacture that the pressure in a bulb through which ions or electrons are travelling, tends to decrease with time.

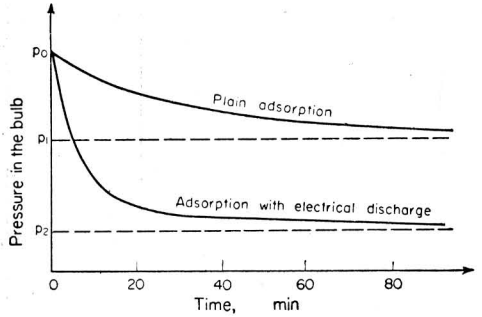


FIG. 4.17

This phenomenon occurring in cold discharges as well as with a thermionic cathode, may be explained as follows:

(a) Gas molecules are ionized by collisions.

(b) By the effect of the electrical field, they go to electrodes opposite to the sign of their own charge (they are mostly positive ions going to the cathode, but with oxygen, negative ions may also be formed).

(c) The ions are then strongly adsorbed on the electrodes; chemisorption may also occur if the gas and the metal have a chemical affinity for each other.

(d) An important fraction of the ions may also be adsorbed on the walls of the bulb, and of course, on the "getter" if there is one.

The pressure decrease in terms of time follows an exponential law. It occurs more rapidly and the minimum pressure is much lower than when it is plain adsorption (without any electrical discharge).

Figure 4.17 illustrates well enough the phenomena in both cases. Times are given only as an indication.

On the other hand, it must not be forgotten that we are not dealing with a pumping effect: the absorbed gases are not evacuated; in particular they are apt to be released as a result of a temperature rise.

These phenomena will be seen again in Vol. II, Sec. 14.5.

CHAPTER V

PRODUCING AND MAINTAINING LOW PRESSURES: PUMPS AND GETTERS

In this chapter, we will study first the devices for the production of the high vacua required for the operation of electron tubes: the pumps.

Then, there will be studied static systems, inserted in electron tubes and which give rise, thanks to their properties of absorption of gases, to the improvement of insufficient vacua and the removal of gases which might be released during the tube life: the getters.

5.1. PUMPS

5.1.1. Quantities characterizing a pump

The performances of a pump are defined by three quantities: the initial pressure, the exhaust speed, and the limiting (or final) pressure.

5.1.1.1. *Initial Pressure (also called fore-pressure)*

Some pumps may directly drive out into atmosphere the gases they extract. On the contrary, for their working, others require first a pressure lower than the atmospheric pressure: they must be backed with a pump of the first type, which, for this reason, is often known as a "fore-pump" or a "backing-pump".

5.1.1.2. *Exhaust Speed of a Pump*

By definition, it will be called *exhaust speed* or *pumping speed* S at a given pressure, the volume of gas extracted by the pump per sec, this volume being measured at the same pressure:

$$S = \left| \frac{dv}{dt} \right|_p . \tag{5.1}$$

For most pumps, this speed varies greatly in terms of pressure. However, there are some pumps the speed of which varies little in a large range of pressures.

(a) *Ideal pump.* Let us study the pressure variations in a vessel as a function of time, the pumping speed being supposed constant. Conversely, we will try to calculate this pumping speed, the law of pressure variation in terms of time being known.

Let V the volume of a vessel containing a gas at a pressure p (Fig. 5.1). The pump being in operation, after a time dt, the volume dv has been extracted and the pressure decreased by dp. As $p\,v$ = constant, this may be written as:

$$pV = (p + dp)\,(V + dv) = p\,V + p\,dv + V\,dp + dp\,dv. \tag{5.2}$$

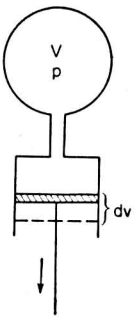


FIG. 5.1

Neglecting $dp\,dv$, it comes:

$$p\,dv = -V\,dp \text{ and } dv = -V\,\frac{dp}{p}. \tag{5.3}$$

Dividing the two parts by dt

$$S = \frac{dv}{dt} = -\frac{V}{p}\,\frac{dp}{dt}.$$

Separating the variables p and t and integrating between two values p_0 and p_1 of the pressure, corresponding to times t_0 and t_1, it becomes:

$$\boxed{S = \frac{2{\cdot}3\,V}{t_1 - t_0}\log\frac{p_0}{p_1}}. \tag{5.4}$$

That is the *Gaede formula*, which allows us to calculate the average exhaust speed of a pump in an interval $(p_0\,t_0)$, $(p_1\,t_1)$.

From this formula, there is obtained the exponential function:

$$p = p_0\,e^{-\frac{S}{V}t} \tag{5.5}$$

giving the law of the pressure decrease in a vessel of a volume V, in which the vacuum is obtained with a pump of a speed S, supposed constant, the initial pressure being p_0 (Fig. 5.2).

Thus, it is seen that, with a theoretically perfect pump (i.e. the speed of which is constant whatever may be the pressure), the pressure can never be cancelled: it is divided by $e = 2{\cdot}718$ every time that time increases by a quantity equal to V/S.

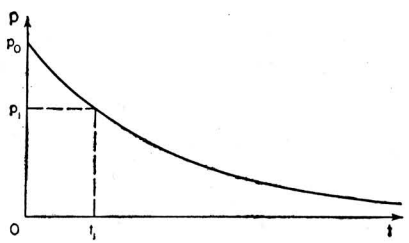


FIG. 5.2

(b) *Actual pumps.* The speed of actual pumps can be considered as constant only in a pressure range the extent of which depends on the particular type of pump. Especially, there is no pump able to give a pressure of zero after an infinitely long time. Any pump presents, owing to its construction or principle, a limiting pressure (Fig. 5.3).

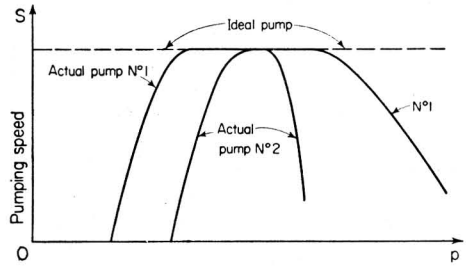


FIG. 5.3

5.1.1.3. *Limiting (or Final) Pressure of a Pump*

Why does a pump show a limiting pressure for which its speed becomes zero? For the following reasons:

1. Owing to the mechanical defects of its construction. It may be mentioned amongst them:

(a) the leaks happening for instance at the pump joints, or even at the axle bearings.

(b) the clearance spaces: these are the parts of the pump, in the neighbourhood of exhausting and escaping orifices, areas in which the gas is not submitted to the evacuation process and consequently keeps a certain residual pressure.

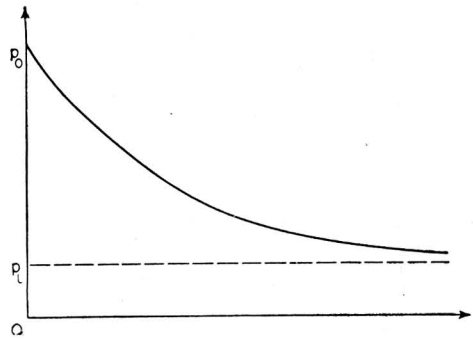


FIG. 5.4

2. Owing to the vapour pressure of the liquids used for lubrication or for the working of the pump itself.

It will be seen how easy it is to remedy this last disadvantage by inserting, between the pump and the vessel to be exhausted, a "cold trap" condensing the troublesome vapours.

From this limiting pressure, it follows that the formula giving the pressure decrease in a vessel in terms of time, becomes:

$$p = (p_0 - p_l)\, e^{-\frac{S}{V}t} + p_l \qquad (5.6)$$

calling p_l the limiting pressure. The curve $p = f(t)$ is then asymptotic not to $p = 0$ any more, but to $p = p_l$ (Fig. 5.4).

Thus, if p_0 and p_l are the values of the pressure at the times t_0 and t_1, the average speed of the pump, in this interval, is given by:

$$S = \frac{2{\cdot}3\ V}{t_1 - t_0} \log \frac{p_0 - p_l}{p_1 - p_l} \quad . \tag{5.7}$$

5.1.2. **Measurement of the speed of a pump**

5.1.2.1. *Constant Volume Method* (Fig. 5.5)

The pump is connected to a vessel of a volume V. A manometer M gives the pressure at every moment. The curve $p = f(t)$ is then plotted, and, applying the Gaede formula, the speed in each interval of time and pressure is determined.

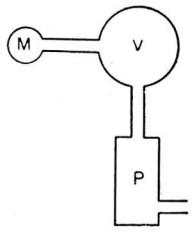


FIG. 5.5

5.1.2.2. *Constant Pressure Method* (Fig. 5.6)

The pump, provided with a manometer M, is connected through a micrometric stopcock to a long glass pipe T, of small diameter.

With the pump working, opening R properly, the quantity of air entering the pump may be regulated so that the pressure at M takes any required value p, between the limiting pressure and the atmospheric pressure.

When the regime is steady at the pressure p, a mercury index is inserted in A, and the time t taken by the latter to traverse the length l is measured. Whence is obtained the volume:

$$v = \frac{\pi d^2 l}{4}$$

measured under the atmospheric pressure, and extracted by the pump under the pressure p.

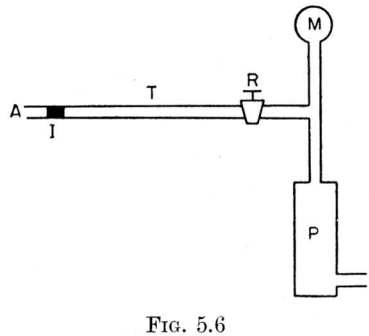


FIG. 5.6

The pump speed (measured under the pressure p mm Hg) is then given by:

$$S = \frac{\pi d^2}{4} \frac{l}{t} \frac{760}{p} \quad . \tag{5.8}$$

5.1.3. Description of pumps

Classification

(a) *Pumps applying Boyle's law*:
- (i) the piston pump;
- (ii) the Sprengel pump;
- (iii) the Gaede mercury rotary pump;
- (iv) the rotary oil pumps (vane pumps);
- (v) the Roots' pump.

(b) *Pumps using gas viscosity*:
- (i) the water-jet pump;
- (ii) the vapour ejector (using water, oil or mercury).

(c) *Molecular pumps*:
- (i) Mechanical molecular pumps (Holweck and Siegbahn);
- (ii) Diffusion pumps (Gaede and Langmuir).

(d) *Pumps using ionization phenomena.*

(e) *Pumps using absorption phenomena.*

5.1.3.1. *Pumps Applying Boyle's Law*

(i) *The piston pump.* This is the oldest vacuum pump, since it was already used by Otto von Guericke in his famous experiments (about 1650). It comprises (Fig. 5.7) a cylinder with two nozzles, one emerging to the atmosphere, and the other to the vessel to be exhausted. Because of the valves s_1 and s_2, at each traversal of the piston, the air exhausted from the vessel is driven out into the atmosphere. The dead space corresponds to the non-zero volume included between the piston when it is at the bottom of the cylinder and the valve s_2. Let v be the volume of this clearance and V the volume of the cylinder. When the piston is at the bottom of the cylinder, the pressure in the clearance is equal to 760 mm Hg. When the piston is at the other end, the pressure p in the cylinder is such as:

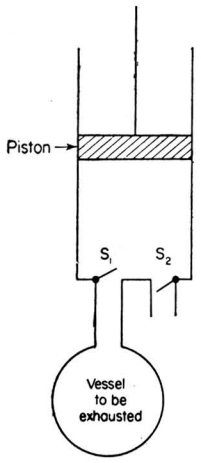


FIG. 5.7

$$v \times 760 = p_1 \times V$$

whence:

$$p_1 = \frac{v}{V} \times 760 \text{ mm Hg}.$$

The valve s_1 can be opened only if the pressure in the vessel is above p_1, which is seen to be the lowest pressure the pump may realize, all the other causes of vacuum limiting being suppressed. At the end of the nineteenth century, these pumps provided with various improvements (oil joints around the piston to improve the tightness, etc.) were used at the beginning of the industrial manufacture of incandescent light lamps.

Their final vacuum is included between 0·1 and 1 mm Hg. Some of them, very big ones, may still be found in old industrial systems. Now these are superseded by rotary oil pumps.

(ii) *The Sprengel mercury pump.* Mercury is dropped into a long vertical tube with a small diameter ($d \leq 2$ mm). It is divided into chain fragments, and between each grain there is a gas bubble enclosed, which is driven down to the atmosphere (Fig. 5.8).

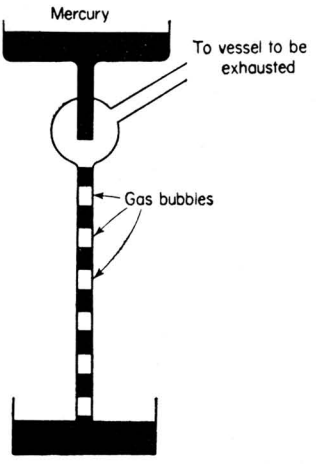


FIG. 5.8

The total height of the mercury drops must be greater than 760 mm.

The pumping speed is low owing to the small diameter of the tube which cannot be increased, because the mercury would not cling to the walls. To remedy it, some pumps have been constructed using several tubes in parallel. Though the limiting vacuum is about the vapour pressure of mercury, this pump is now given up.

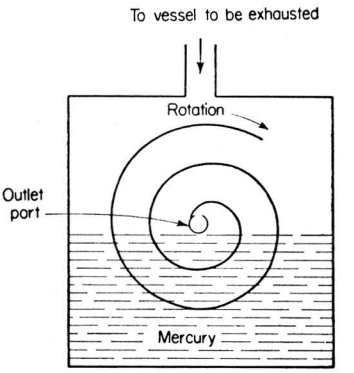


FIG. 5.9

(iii) *The Gaede mercury rotary pump.* This pump was in favour at the beginning of this century for the pumping of lighting-bulbs (Fig. 5.9).

Consider the surface of sheet-iron obtained by moving a spiral curve perpendicularly to its plane. This is then made to rotate around its horizontal axis, being half-immersed in a mercury pool. Thus the gas is driven from the end of the spiral

to the axis, from which it is evacuated. A rough fore-vacuum (such as the vacuum obtained with a water-jet pump) is required to avoid the mercury going up the pumping circuit under the effect of atmos-

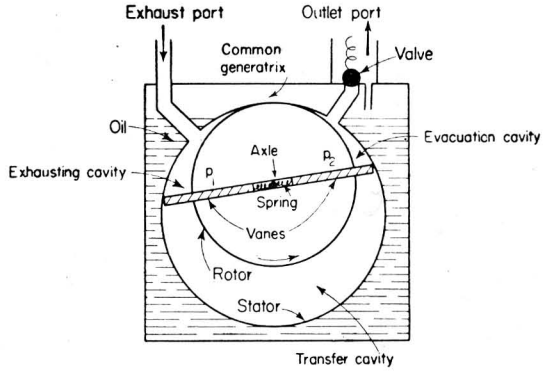


FIG. 5.10

pherical pressure. The vacuum is only limited by the vapour pressure of mercury.

(iv) *Rotary oil pump* (*vane-type pump*). We will deal more fully with this because it is very commonly used.

Description. The rotary oil pump comprises two cylindrical elements: a rotor rotating inside a stator, the rotor-diameter being less than that of the stator. Further, the rotor and the stator are tangential to one another along the generatrix M (Fig. 5.10).

The stator has two orifices, known as exhausting and evacuation orifices. As for the rotor, it has a diametral slit in which two vanes P_1 and P_2 are sliding with low friction; a central spring pushes these vanes against the stator walls.

The vanes separate three cavities between the rotor and the stator: exhausting, transfer and evacuation cavities.

Let us study the working: when the rotor revolves in the direction of the arrow, the volume of the exhausting cavity rises, which makes the pressure decrease in the vessel connected to it. Then, when the vane P_2 has passed over the generatrix M, the exhausting cavity becomes the transfer cavity by which the gas is conveyed from the inlet to the outlet of the pump. Finally, when P_1 passes over the evacuation orifice, the transfer cavity becomes the evacuation cavity, and the gas is thrown out into the atmosphere. In the mean-

time, a new exhausting cavity is formed with P_2 and the cycle begins again.

Volumes included between each orifice and the common generatrix M are dead spaces. In fact, in the right one, gases are strongly compressed, whilst a high under-pressure occurs in the left one: thus, leaks result along the generatrix M.

To remedy this, it would be required to reduce as much as possible the angle made by the two orifices, by bringing them close to M. The disadvantage would be to slow down the gas-flow considerably. This is the reason why it is preferred to make the stator and the rotor as secants and not tangents (Fig. 5.11). The dead spaces are suppressed without too strong a resistance being opposed to the circulation of gases.

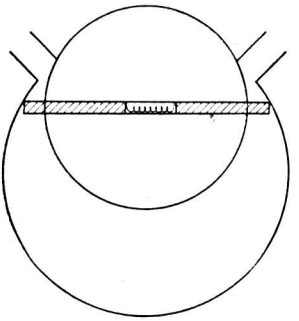


FIG. 5.11

Strictly speaking, this pump does not require the presence of a valve. However, it is useful to place one on the evacuation orifice, because the mean pressure is thereby reduced in the evacuation cavity, and consequently the risk of leaks along the common generatrix (or along the part of the cylinder common to both the rotor and the stator) is diminished.

This can be checked by drawing the curves $p = f(t)$ of the pressure in terms of the rotor rotation, in the exhausting cavity and in the evacuation cavity (Fig. 5.12)† respectively.

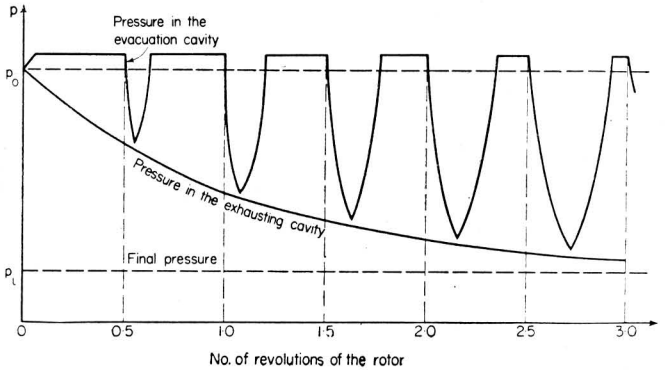


FIG. 5.12

† G. A. Boutry (1).

It is seen that:

(a) the pressure in the exhausting cavity regularly decreases according to the well-known exponential law;

(b) in the evacuation cavity, when gases begin to be expelled, the pressure slightly exceeds the atmospheric pressure p_0, by the quantity required for the lifting of the valve. But the period of time during

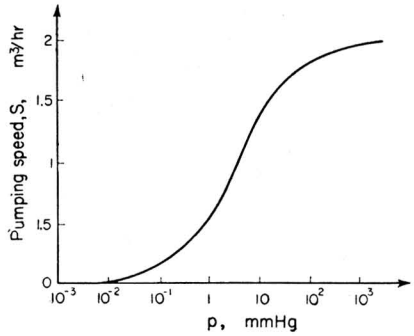


FIG. 5.13

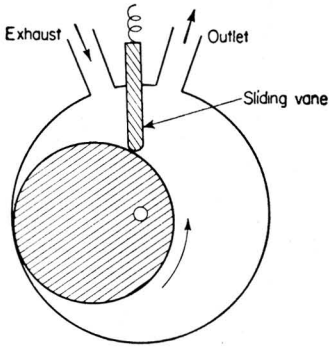


FIG. 5.14

which this occurs decreases at each cycle, and, when the limiting pressure is reached, the valve does not go up any more, as there is no more gas to expel. At this time, the pressure in the evacuation cavity is as low as in the exhausting cavity, and it cannot produce leaks any more along the tangency-generatrix.

Greasing and air-tightness are obtained by oil contained in a tank in which the system is immersed: oil enters the pump, owing to atmospheric pressure, through the bearings, and it is expelled through the valve, from whence it falls again into the tank.

Characteristics of rotary oil pumps. The smallest ones have a pumping-speed of 2 m³/hr at 0·1 mm Hg. The biggest ones reach, at the same pressure, 2000 m³/hr. The power of the motor is, respectively, 150 W and 10 kW, with a rotation speed of 300 to 500 rev/min.

Figure 5.13 gives a typical curve of the pumping speed in terms of pressure. The limiting pressure reaches 10^{-2} mm Hg with a pump in a good state of working. With two pumps in series, it may be reduced to 10^{-3} mm Hg.

Alternative forms of the rotary oil pump

1. *The single-vane type pump.* Figure 5.14 illustrates the principle of this pattern. The axle of rotation is concentric with the stator, but

eccentric to the rotor, so that when the latter rotates, it remains in contact with the former by the contact-generatrix M which revolves at the same time. Here, a single vane is used which can only slide vertically, so forming between the rotor and the stator two cavities, the one of exhaust, the other of evacuation.

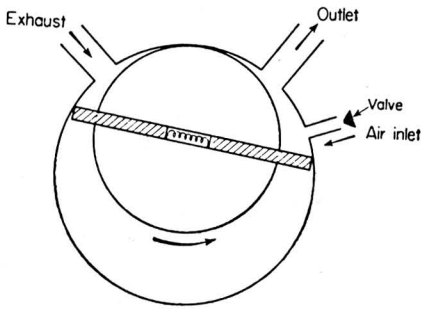


FIG. 5.15

2. *The air-ballast pump.* Consider the working of the rotary oil pump. When the pressure has decreased to about the final vacuum, the extracted gas must be compressed up to a ratio of, say, 1000 or 10,000, in order to be expelled into atmosphere. If one has to evacuate a vessel containing some water or other liquids with high vapour pressure, these vapours are condensed during compression. Then the liquids formed emulsionize with oil, so making the limiting pressure very bad. To avoid this, the air-ballast pump was designed by Gaede (Fig. 5.15). An orifice communicating with the atmosphere allows air to enter the transfer cavity at such a time that the compression ratio does not exceed about 10. Combined with the temperature increase of the inner part of the pump, this prevents vapours from condensing and leads them to be expelled with the admitted air.

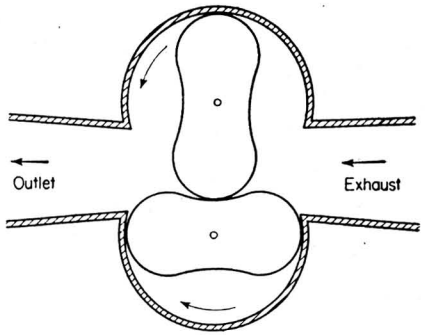


FIG. 5.16

The air-inlet can be adjusted by a valve, which allows the air-flow to be controlled and even completely stopped. In this last case, the pump works, of course, as an ordinary rotary oil pump.

(v) *The Roots' pump.* This pump, recently designed, gives considerable flows at pressures of about 10^{-2} mm Hg, which is the intermediate range between that of rotary oil pumps and diffusion pumps. They compete with steam-ejectors described in Sec. 5.1.3.2. The rotor is formed with two 8-shaped lobes, rolling one over the other without

any sliding (Fig. 5.16). Between these lobes and the stator, transfer cavities are created, expelling the gas from the exhausting region to the evacuation region. The limiting vacuum of these pumps being around 10^{-4} mm Hg, their way of working is probably similar to the rotary oil pump for high pressures, and is near to the working of the mechanical molecular pumps at low pressures (see Sec. 5.1.3.3).

On the same pattern, some pumps are now constructed, with speeds going from 500 to 5000 m^3/hr at 10^{-2} mm Hg. They are mostly used for the melting of metals under vacuum.

5.1.3.2. *Pumps using Gas Viscosity*

These pumps are based upon the following principle, of which the physical aspect has been studied in Chap. II, Sec. 2.4.2:

If a fluid, a gas or a liquid, moves inside a pipe of variable diameter, in certain conditions, a point of this tube may be found at which the pressure is lower than anywhere else. This gives the possibility of connecting this point to a vessel to be exhausted and thus obtaining its evacuation by entraining the emulsified gas in the fluid.

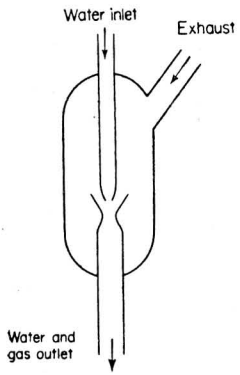


FIG. 5.17

(i) *The water-jet pump.* A strong water jet, at a pressure of a few kg, passes through a nozzle and issues into a conical opening (Fig. 5.17). Around the liquid jet a gaseous sheath is formed driven by viscosity. When the thickness of this sheath is sufficiently reduced, it emulsifies in the water and takes away the gas bubbles. This pump cannot give pressures lower than a few cm of mercury: in fact, the pressure of water vapour at 20°C is of 17 mm Hg.

It is commonly used in chemistry laboratories to accelerate filtrations.

(ii) *The steam-ejector.* The water-jet may be replaced by a jet of water, oil or mercury vapour. It may be recalled that the water-steam system has been used for a hundred years on railway engines to supply the boiler with water issuing from the tender: this is the "Giffard injector", in which the vapour issuing from the boiler brings about the required depression to draw the water out of the tank and to force it into the boiler.

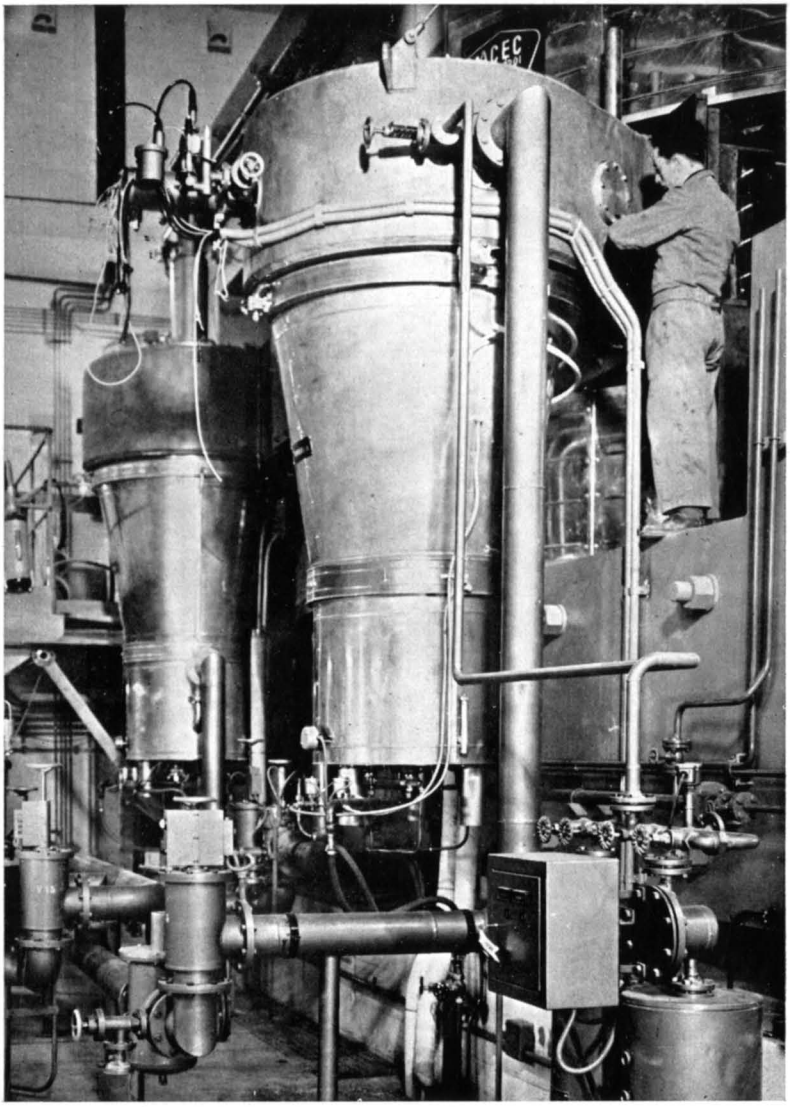
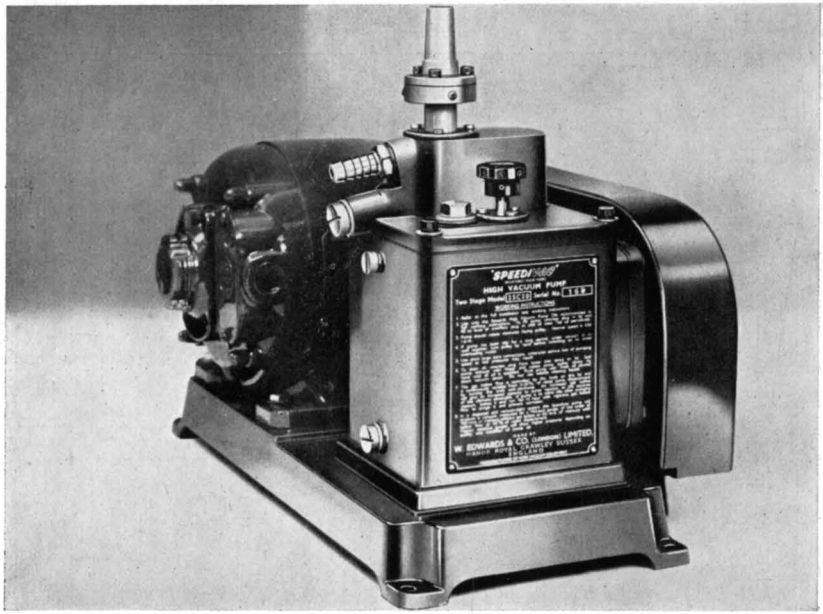
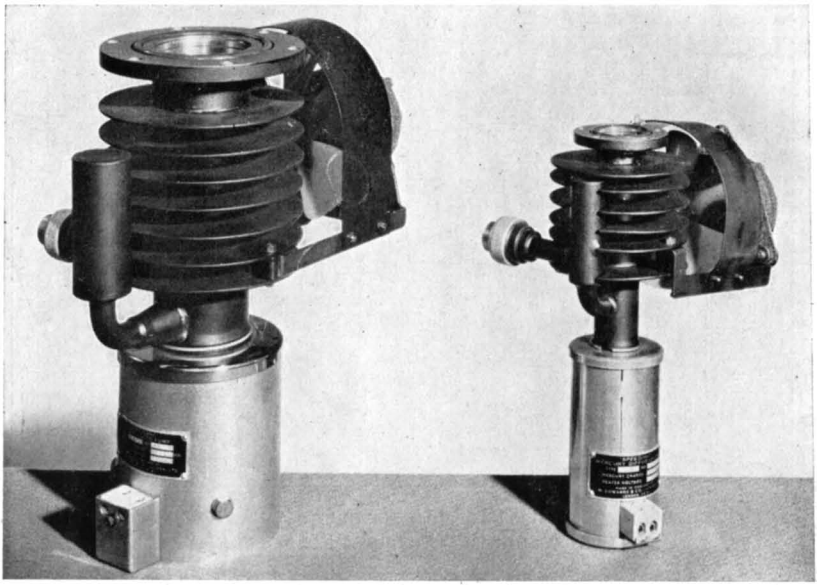


Plate 1. LEYBOLD type DO 20002 oil diffusion pumps (pumping speed: 20,000 l./sec). These pumps are used to exhaust the synchrocyclotron of the C. E. R. N., Geneva (Courtesy C. E. R. N.)



(a)



(b)

Plate 2. (a) EDWARDS type 2 SC 20 rotary oil pump. Pumping speed: 10 m³/hr. Ultimate pressure: 5×10^{-3} mm Hg
(b) EDWARDS air-cooled mercury diffusion pumps. (Courtesy W. Edwards and Co. Ltd., London, England)

At present, these water-steam systems are used to produce depressions of some cm Hg with very high flows. For example, mineral-oil refineries employ steam ejectors, each consuming 150 kg of steam per

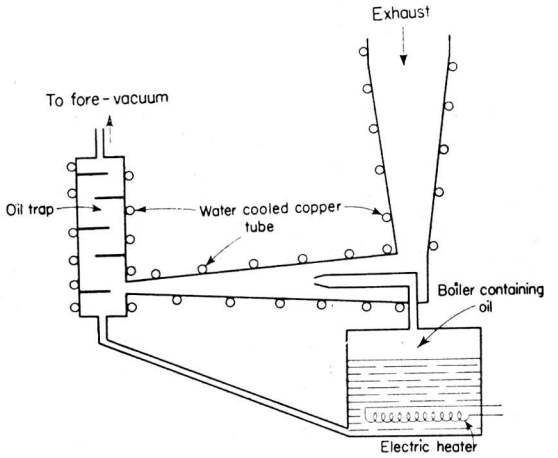


FIG. 5.18

hour under a pressure of 35 kg/cm². A vacuum of 70 mm Hg is thus achieved, sufficient to make the distillation of oil by-products easier. Each unit treats 2000 tons of heavy products per 24 hr, from which 50 tons of light products are recovered.

At the moment, several manufacturers have put on the market "booster pumps" (intermediate pumps); they comprise an oil vapour ejector system (Fig. 5.18).

The main advantage of these pumps is that they have a very high pumping speed at about 10^{-1} or 10^{-2} mm Hg, i.e. in a pressure range in which rotary oil pumps are in the neighbourhood of their limiting vacuum, whilst diffusion pumps give their maximum speed only at lower pressures. (See "association of pumps", Chap. VII.)

For these pressures, these pumps have speeds which go from 50 to 1500 l./sec, according to their size. For backing, they require a starting pressure of 3 mm Hg. Their limiting vacuum is 10^{-4} mm Hg. The required heating power lies between 1·8 and 6·5 kW. The oil boiler contains from 1·5 to 10 l. of oil.

5.1.3.3. *Molecular Pumps*

While the above pumps are working as if the gases to be extracted might be considered as continuous fluids, the working of molecular pumps can only be explained if gases are comprised of elementary particles. They apply then the principles of kinetic theory.

(i) Mechanical Molecular Pumps.

Principle. These pumps operate on the principle of contacting the gas molecules to be expelled with a wall moving at a high speed, so that each molecule coming into collision with it receives an impulse directed towards the fore-vacuum.

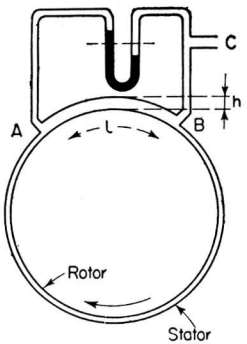


Fig. 5.19

Consider a smooth drum rotating in a steady cylinder with a very small clearance (Fig. 5.19).

On a circular arc of a length l, a channel AB is arranged with a straight section s, and a height h; each end of this channel is connected with a manometer. Through an orifice C a vacuum may be made, in order to make the mean pressure vary in the channel.

The cylinder rotating in the clockwise sense, the pressure in A is seen to decrease, while the pressure in B rises.†

Let us calculate this variation of pressure in terms of the parameters of the system. Two cases may be considered, according as the flow is viscous ($L \ll h$) or molecular ($L \gg h$). (L is the mean free path).

As only the form of the phenomena and their orders of magnitude are in question, it is reasonable to apply to the channel AB, the section of which is rectangular, the formulae obtained for the flow of gases through cylindrical pipes.

† The working of this pump may be explained as follows. Suppose the cylinder to be motionless. The molecules coming from A, colliding with the drum, rebound in any direction, as it is assumed there is no reflection as for a billiard ball, but rather fixation of the molecules, and then re-evaporation not long after (see Sec. 2.2.9). If the cylinder rotates, rebounding molecules have a component of velocity directed towards B.

(a) *Viscous flow*

To simplify, instead of considering the wall as moving with respect to the gas, the gas is supposed to move with relation to the wall. The flow in volume is (from eq. (2.107)):

$$D_v = \frac{\pi r_0^4}{8 \eta l} (p_B - p_A) = \frac{s^2}{8 \pi \eta l} (p_B - p_A) \tag{5.9}$$

(s = channel section AB).

On the other hand:

$$D_v = s u \tag{5.10}$$

u being the relative speed of the gas with respect to the wall (or conversely); then it follows that:

$$p_B - p_A = \frac{8 \pi \eta l u}{s} . \tag{5.11}$$

This shows that the difference of pressure is independent of the mean pressure in the channel.

For instance, if $p_B = 760$ mm Hg is the initial pressure, a value of u, linear speed of the drum, may be taken such that $p_A = 750$ mm. It might be thought that in the same conditions, a fore-vacuum of 10 mm in B would be enough to obtain a zero pressure in A. This would be wrong because, for low pressures, the viscous flow gives way to the molecular one.

(b) *Molecular flow*

In this case, the flow in volume is given by:

$$D_v = \frac{8 r_0^3 (p_B - p_A)}{3 l p} \sqrt{\left(\frac{\pi k T}{2 m}\right)} \tag{2.117}$$

with:

$$p = \frac{p_B + p_A}{2} \text{ and } D_v = s u.$$

It is then found that what is independent of the mean pressure p, is no longer $p_B - p_A$, but p_A/p_B:

$$\frac{p_A}{p_B} = \frac{1 - \frac{3}{4} \pi u l \sqrt{\left(\frac{2 M}{s R T}\right)}}{1 + \frac{3}{4} \pi u l \sqrt{\left(\frac{2 M}{s R T}\right)}} . \tag{5.12}$$

From the above, the following conclusions can be deduced:

1. It is obvious that p_A/p_B may become as small as desired, provided that u, linear speed of the drum, is increased.

2. Clearly, if the linear speed of the drum became higher than the mean speed of the molecules, only a few of them should come backwards, and the extraction should be excellent. For that, linear speeds greater than 500 m/sec should be reached. Fortunately the working is already found to be satisfactory for $u \approx 100$ m/sec.

3. At these relatively low speeds, the pump will be more efficient the more frequently the molecules to be driven out are in contact with the rotating drum. For that the mean free path must be high compared with the height h of the channel. It is consequently necessary to achieve a fore-vacuum.

4. The ratio p_A/p_B is, according to the mechanical perfection of the pump and to the rotation speed, included between 10^{-5} and 10^{-7} (for instance, a limiting pressure of about 10^{-6} mm will be obtained with a fore-vacuum of about 1 mm).

5. The speed of a mechanical molecular pump varies proportionally to the square root of the mass of the molecules. In fact, the mean energy of the molecules is known to be dependent only on the temperature, and for two different gases, at the same temperature, this may be written as:

$$m_1 c_1^2 = m_2 c_2^2. \tag{5.13}$$

Now, the principle of this pump is precisely to give to molecules an extra momentum, so that it may be written:

$$\frac{S_2}{S_1} = \frac{c_1}{c_2} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{M_2}{M_1}} \tag{5.14}$$

(S_1 and S_2 represent the exhaust speeds for each gas).

It is easily understood how this property is used in nuclear physics for the separation of isotopes (bodies with the same chemical properties, but with different masses).

The Holweck molecular pump.

Though Gaede is the inventor of the mechanical molecular pump (1912) and though his pattern has been in use, we will only discuss the pump Holweck discovered and constructed in 1922. It has a simpler execution than that of Gaede.

It involves a smooth rotating drum (Fig. 5.20) and a stator, with a clearance between them not exceeding 0·03 mm.

In the stator, helical channels are made, the depth of which increases from the sides (0·5 mm) to the centre (12 mm). These channels shape two helical grooves, with inverse pitches, on both sides of the median

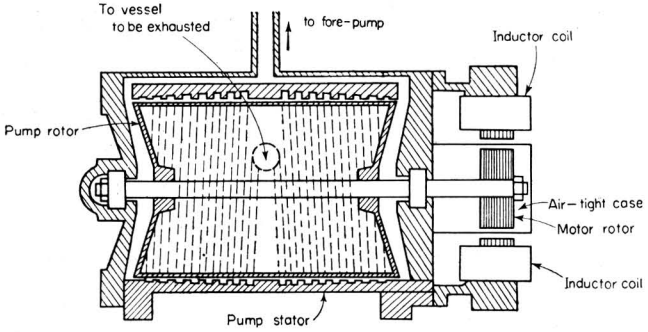


FIG. 5.20

plane. The fore-vacuum is applied at the sides, and the high vacuum is obtained in the centre.

To avoid leaks, the drive of the rotor is made by an induction motor the stator and the rotor of which are separated by an air-tight case made of thin copper. The rotor is fitted with ball-bearings.

Characteristics:

rotor: diameter 150 mm; length 220 mm;
rotation-speed: 4500 rev/min;
electric power of the motor: 10 W;
pumping-speed, nearly constant between 0·1 and 0·001 mm: 2500 cm^3/sec;
limiting-vacuum: about 10^{-6} mm Hg;
fore-vacuum: about 20 mm Hg.

The Siegbahn molecular pump.

Invented in 1926 and improved in 1946 by Gondet.† The rotor is a smooth disk, and the grooves in which gas travels form two plane spirals on both sides of the disk (Fig. 5.21).

diameter of the disk: 40 cm;
rotating speed: 4200 rev/min;
fore-vacuum: 0·05 mm;
pumping speed: 150 l./sec at 10^{-4} mm Hg;
limiting vacuum: about 10^{-6} mm Hg.

† *Le Vide*, No. 18, p. 513.

Advantages and disadvantages of the mechanical molecular pumps

Advantages:

(a) Immediate starting.

(b) No traps necessary, because of the absence of oil or mercury.

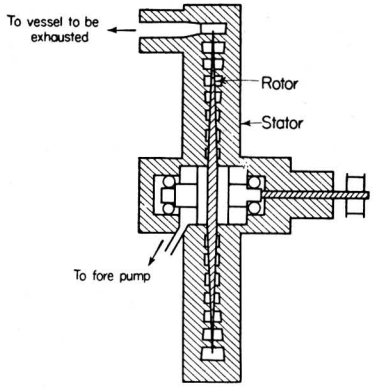


FIG. 5.21

(c) Different speeds according to the gas (this allows them to be used for the separation of isotopes).

Disadvantages:

(a) Very high mechanical precision, hence a very high price.

(b) Brittleness and risk of damage in case of accidental introduction of solid particles in the vacuum system (glass, metals, etc.).

(ii) DIFFUSION PUMPS

Principle. The principle of these pumps has been stated by Gaede in 1915. They are molecular pumps in which the impulses directing the molecules of the gas to be exhausted to the fore-vacuum, are obtained thanks to the collisions with the molecules of a vapour called the *pumping fluid.*

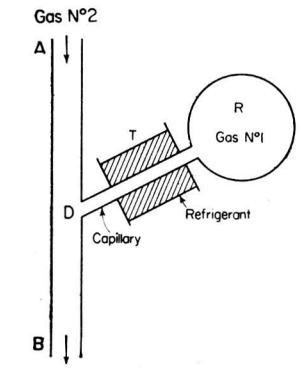


FIG. 5.22

Let R be a vessel containing the gas 1 to be removed. It is connected by a capillary pipe† to a tube AB in which the gas 2 (the pumping fluid), easily condensable, is flowing (Fig. 5.22).

At the orifice D of the capillary, diffusion of both gases takes place one into the other. Without any special precaution, the gas 1 is gradually entrained by the gas 2, which takes its place in the vessel R.

† A capillary is a pipe the diameter of which is small compared with the mean free path.

Now, suppose the capillary to be cooled, with the help of a refrigerant, to a temperature T, such that the gas 2 but not the gas 1 is condensed. The latter will diffuse into the gas 2 and consequently is driven out by it; but the gas 2 cannot take its place in the vessel R, because it will be condensed at the contact with the cooled walls of the capillary. The pressure in R will decrease till it reaches the vapour pressure of the gas 2 at the temperature of the refrigerant.

It is readily understood why the tube connecting R to the circuit AB must be "a capillary": the molecules of the gas 2 must have the greatest opportunity to meet the walls and to be condensed before reaching R.

Gaede showed that, so long as the capillary diameter is small compared with the mean free path, the pumping speed of such a system has to a first approximation the value:

$$S = \frac{\pi v_m d^3}{12 l} \tag{5.15}$$

d and l being respectively the diameter and the length of the capillary pipe and v_m the mean speed of the gas in the capillary pipe. This is nothing other than the *conductance* of the capillary in molecular flow (see Chap. VII, Sec. 7.1.6). The following conclusions may be deduced:

(a) The pumping speed is constant in terms of the pressure when molecular flow is reached.

(b) The pumping speed is very small. For instance with a capillary of a length of 10 cm and a diameter of 2 mm, S is found to be about 10 cm^3/sec. In fact, it is about the speed Gaede obtained in his first experiments.

(c) Such a pump requires a fore-vacuum which allows one, by reducing the pressure, to increase the mean free path and to increase also the diameter of the capillary.

(d) The pumping speed, to a first approximation, does not depend on the nature of the gas 2 used for the driving.

(e) The limiting pressure is theoretically zero (as the speed does not depend on the pressure). In fact, S is limited:

1. by the vapour pressure of the gas 2 at the temperature of the refrigerant.
2. by the back-diffusion of the gas 2 in the vessel R, a diffusion impossible to suppress entirely, the kinetic theory foreseeing

that there is always a small probability for these molecules to pass through the capillary without being condensed.

In conclusion, the Gaede system, though of a high theoretical interest, is in practice unusable as it is, owing to the presence of the capillary which considerably slows down the pumping-speed.

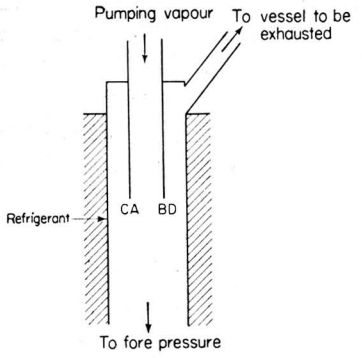


FIG. 5.23

Langmuir's diffusion and condensation pump.†

In 1916, Langmuir thought of taking away the capillary, and to set the system so that in addition to the mutual diffusion, there is a driving of the molecules of the gas 1 by those of the gas 2. The gas 2 is supposed to emerge from the nozzle AB with a certain speed, and the pressure is supposed to be such that the mean free path of the gas at the output AB is of the same order as the distance between the nozzle AB and the external tube which is well refrigerated (Fig. 5.23).

In these conditions, the gas 2 is condensed on the walls CD before being able to go back to the vessel to be exhausted. But, before this condensation, there was first a mutual diffusion of the gases 1 and 2, and also a driving down of the gas 1 by the gas 2.

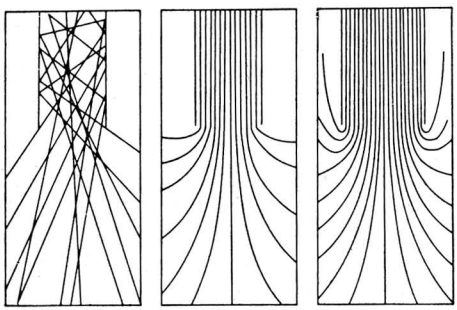


FIG. 5.24

After the condensation of the gas 2, the gas 1 is removed by the fore-vacuum.

Let us show why, in this Langmuir system, it is of real interest to have the distance between the pipe AB and the external pipe CD of the same order as the mean free path:‡

(a) Let us suppose firstly (Fig. 5.24a) the pressure is

† A detailed study of this pump has been made by MATRICON, *Journal de Physique*, March 1932.

‡ After A. L. Reiman, *Vacuum Technique*, Chapman and Hall, London.

very low and the flow of the gas 2 is molecular. The number of collisions between the gas 2 and the gas 1 to be driven is very small. The gas 1 will therefore not be driven, or only very slightly.

(b) In the opposite case, the pressure is supposed to be very high (low mean free path, Fig. 5.24c). Owing to the high number of collisions, the gas 2, when emerging from the nozzle AB, will diffuse in all directions, consequently also towards the top. An important proportion of this gas will not be condensed on the cold wall CD and will then take the place of the gas in the vessel.

(c) Lastly, if the pressure is such that the mean free path is of the same order as the distances AC and BD, the number of collisions between the molecules of the gas 2 and of the gas 1 is high enough for the diffusion and the carrying away to be operative; however, the gas 2 is condensed on the wall CD quickly enough to prevent it from going up again (Fig. 5.24b).

As a summary, the conditions for a good working of the Langmuir pump are:

(a) that the highest number of collisions possible must occur between the molecules of the gas 2 (the pumping fluid) and these of the gas 1 (the gas to be removed).

(b) that on the average, these collisions tend to carry the molecules of the gas to be removed towards the fore-vacuum.

(c) that the smallest possible number of the molecules of the pumping fluid may go up to the vessel to be exhausted.

Finally, experience shows that the Langmuir pump has the following characteristics:

1. The pumping speed is constant only in a small range of pressures corresponding to a mean free path of the order of the difference between the radius of the central nozzle and the external cooled tube. It decreases on both sides of this.

2. This exhaust speed is about 100 times higher than the speed of the Gaede pattern: say, about 1 l./sec for a difference of radii of about 1 mm, with a diameter AB of about 10 mm.

3. The initial pressure, all other things being equal, may be higher than the one required in the Gaede pump, i.e. it may be about 1 mm Hg.

Practical Construction of Diffusion Pumps

Mercury Vapour Pumps.

From the outset, the most commonly used pumping fluid in diffusion pumps has been mercury vapour. For this application, mercury has numerous advantages:

(a) Liquid at ordinary temperature, it boils, under a vacuum of 1 mm Hg, at a relatively low temperature: about 120°C.

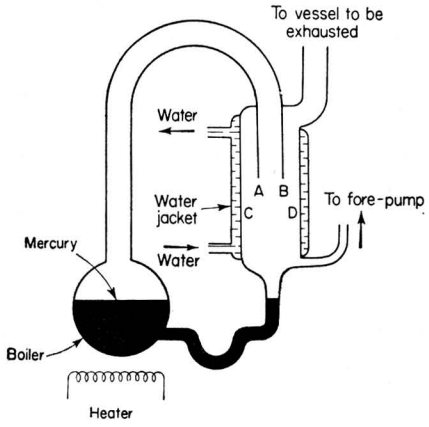


FIG. 5.25

(b) Heavy and not "wetting" the walls, it easily travels inside the pumps and does not dirty them.

(c) The heat of formation of its oxides is low, so that the oxides formed are easily dissociated in vacuum: the mercury pump can well support short exposures to air during operation.

(d) The liquid mercury is a good heat conductor, so that the boilers of the pumps have simple structures.

(e) The mercury vapour is easily condensed by cooling at 20°C, and the vapour pressure at this temperature ($\approx 10^{-3}$ mm Hg) is low enough for many applications.

These pumps may easily be made either of glass for laboratories, or of metal for industrial purposes.

A. *Glass pumps.* The plainest type is represented in Fig. 5.25. Mercury is heated in a boiler by an electrical heater or a bunsen burner. Mercury vapour goes up a heat-insulated glass tube, and then comes down again through the nozzle AB, at which diffusion occurs with the gas coming from the vessel to be exhausted. This gas is then driven to the lower part by the collision of its molecules with the molecules of the mercury vapour. The latter are condensed on the walls, cooled by a water-jacket, while the gas to be removed is evacuated by a fore-pump (usually a vane-type rotary oil pump).

As for the condensed mercury, it is brought back to the boiler by a syphon. The fore-pressure must be of about 1 mm Hg.

Prof. Louis Dunoyer proposed a pump, also made of glass, which, in addition to the diffusion stage, possessed on the side of the fore-vacuum, an ejector using a part of the vapour stream produced by the mercury boiler (Fig. 5.26). Owing to this arrangement, the pressure given by the fore-pump need only be as high as 5 to 10 mm Hg.†

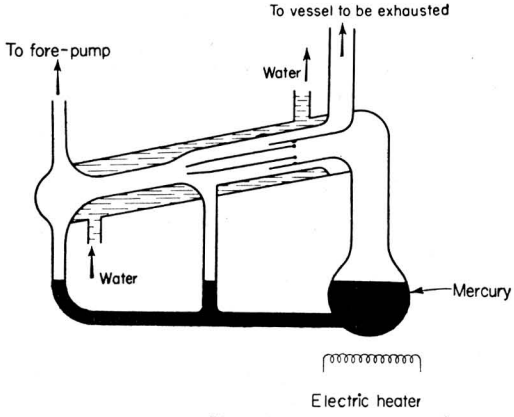


FIG. 5.26

This combination of a diffusion stage with an ejector working by viscosity, has later become general on most industrial pumps.

These pumps, easily constructed by a good glass-blower, have for example the following characteristics:

diameter of the nozzle AB: about 3 cm;
diameter of the tube CD: about 4 cm;
weight of mercury: 1 kg approximately;
electric power of the heater: 2 to 300 W;
pumping speed at 10^{-2} mm Hg: a few l./sec.

B. *Metal pumps.* An arrangement with a symmetry of revolution round an axis is generally used (Fig. 5.27).

The boiler, located at the lower part, is formed with by coaxial cylinders between which the mercury is located. The heater (a steatite cylinder bearing a nickel–chromium coil-spring) is inserted in the inner cylinder.

After having risen up in the axial tube, the mercury vapour is thrown back to the lower part thanks to a diffusion umbrella, followed

† This apparatus behaves exactly as if a "booster-pump" were systematically used, integrating it into the diffusion pump (see Sec. 5.1.3.2).

by an ejector (the throttle of the latter corresponding to the cooled wall of the pump).

The whole forms a device easy to dismantle for cleaning.

It will be noticed that the fore-vacuum is applied with the help of a water-cooled coil, in order to avoid the driving of mercury vapour into the rotary oil pump.

The smallest of these pumps have a height of 30 cm and a diameter of 7 cm. Their pumping speed at 10^{-2} mm lies between 3 to 5 l./sec.

The biggest ones have a diameter of 80 cm and a height of 2 m. They reach an exhaust speed of 10,000 l./sec.

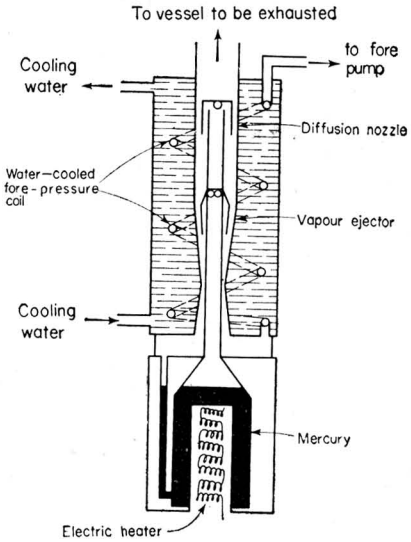


FIG. 5.27

They are made of iron or stainless-steel. Copper is not suitable, because it amalgamates with mercury.

When a pump has been working for some hundred hours, a decrease of the pumping speed generally occurs, added to a rise of the limiting pressure. This is due to a contamination of the pump by greases, oils, etc., coming from vapours extracted from vessels to be exhausted. It is then required:

1. To empty out the dirty mercury.
2. To clean the pump carefully with an organic solvent (such as benzene, xylene, etc.) and then to dry it with hot air.
3. To put back in the boiler some distilled mercury (see Sec. 8.2).

Besides the above advantages offered by mercury vapour used as a pumping-fluid, it is fair to mention some disadvantages:

(a) without any special care, the vacuum given by a mercury diffusion pump is limited to about 10^{-3} mm Hg, which is the vapour pressure of mercury at 20°C. This vacuum is frequently insufficient.

(b) to obtain a lower pressure, it is necessary to place between the pump and the vessel to be exhausted a "freezing-trap" (see Sec. 7.3.3)

in which the mercury vapours are condensed. If the refrigerant is dry ice (−78°C), the limiting pressure may be, in principle, reduced to 10^{-9} mm Hg. With liquid air, it should be possible to go down to 10^{-22} mm Hg, which value is of course quite utopian.

But the use of a freezing-trap offers two disadvantages:

(i) it requires a supply of cooling agent, which is not always easy;

(ii) the presence of the trap reduces the pumping-speed (see Sec. 7.3.3).

Oil Diffusion Pumps.

For twenty years it has been attempted to replace mercury by a liquid having a vapour pressure lower than that of mercury at 20°C. Various oils are now used.

A. *Qualities required of oils for pumps*

The oils employed must have the following characteristics:

1. Their vapour pressure must be, at 20°C, as low as possible to avoid the use of a freezing-trap.

2. They must be stable, in spite of the combined use of low pressures and high temperatures.

3. They must have, in the liquid state, a low viscosity to come back readily to the boiler after their condensation.

The conditions 1 and 3 are a little contradictory, because generally the thickest oils have indeed the lowest vapour pressures. Fortunately, there are some exceptions.

B. *Different types of oils for diffusion pumps*

(a) *Oils arising from petroleum refining.* These are generally known under the name of Apiezon oils.†

The most interesting, Apiezon B oil, shows the following characteristics (see also the curve of Fig. 4.3):

vapour pressure at 20°C: 3×10^{-7} mm Hg;

boiling temperature under 0·1 mm Hg: 160°C;

boiling temperature under 1 mm Hg: 200°C.

(b) *Phthalic and sebacic esters.* By making phthalic acid $C_6H_4(COOH)_2$ or sebacic acid $C_8H_{16}(COOH)_2$ react with a saturated alcohol, one obtains butyl, amyl, etc. phthalates and sebacates.

Mostly octyl phthalate is used (commercial name: Octoil), of which the formula is: $C_6H_4(CO_2C_8H_{17})_2$; and octyl sebacate (named Octoil S), of which the formula is: $C_8H_{16}(CO_2C_8H_{17})_2$.

† Registered trademark of Shell Chemicals Ltd.

Their characteristics are the following:

	p_0 at 20°C	Boiling temperature (°C)	
		at 0·1 mm Hg	at 1 mm Hg
Octoil	2×10^{-7} mm Hg	155	190
Octoil S (See Fig. 4.3)	2×10^{-8} mm Hg	170	210

(c) *Silicone oils.* They are methyl polysiloxanes formed by joining two or three of the following radicals:

$$(CH_3)_2SiO$$
$$(CH_3)SiO_{3/2}$$
$$(CH_3)SiO_{1/2}.$$

Especially the following products, made by Distillation Products Inc. are used:

Name	p_0 at 20°C	Boiling temperature (°C)		
		at 0·1 mm Hg	at 1 mm Hg	at 760 mm Hg
DC 702	10^{-8} mm Hg	145	190	400
DC 703	10^{-10} mm Hg	210	250	430

The interest in silicone oils lies:

in the extremely low pressure which they can achieve without any freezing-trap; (however, see Vol. II, sec. 15.2.1);

in their remarkable strength against thermal decomposition, as well as against the action of air upon the hot oil.

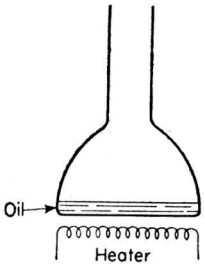


FIG. 5.28

C. *Construction of oil diffusion pumps*

Though their working principle is identical to that of mercury diffusion pumps, their construction requires some differences with respect to the latter, owing to the physical and chemical properties of oils.

1. Oils having a low thermal conductivity, the boilers must be fashioned in order to have a large heating surface. Oil is thus spread in the lower part of a flat-bottomed glass reservoir (Fig. 5.28). The heating-resistor may also be immersed, protected by a glass tube. Similar arrangements are used in metallic pump.

2. Oils having a density lower than that of mercury, projection of oil drops into the high-vacuum circuit must be avoided. For that reason, at the top of the pump a screen is set which stops oil drops while slowing as little as possible the gas flow. For example, this may consist of baffle-plates, spiral screens or concentric flat rings of regularly variable diameter (Fig. 5.29).

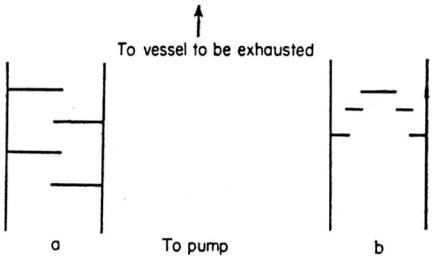


FIG. 5.29

3. As oils are complex organic substances, under the combined effect of the underpressure, of the rise in temperature and of the chemical effect of gases, they always undergo a decomposition resulting in the production of substances of high vapour pressure, which brings about a raising of the limiting-pressure.

Consequently, to reduce this tendency to "cracking", it is necessary to back oil diffusion pumps with a fore-vacuum much below the pressure used on mercury diffusion pumps: 10^{-1} to 10^{-2} mm Hg.

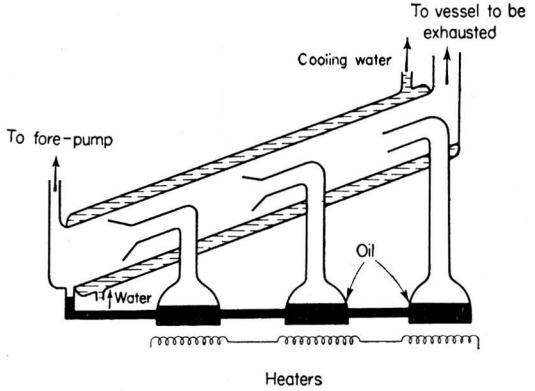


FIG. 5.30

Besides, care must be taken to avoid admission of any air to the hot pump (however, supporters of silicone oils positively state these are not sensitive to this kind of trouble).

4. Finally, to remedy the increase of the limiting-pressure due to the "fatal" decomposition of the pumping oil, oil diffusion pumps are often constructed so that the products of decomposition which are the most volatile are stored in a region of the boiler connected to the fore-vacuum and not to the high vacuum. These pumps are called *fractionating oil diffusion pumps.*

Figure 5.30 gives the diagram of the principle of such a pump: the pump is provided with three distinct boilers. After the condensation, oil comes back to the boilers through a single tube and has to pass successively through each of the boilers, beginning with the one which supplies the stage on the side of the fore-vacuum, and ending up with the stage corresponding to the high vacuum. Thereby the most volatile parts of the oil are evaporated on the side of the highest pressures, and only the compounds with a low vapour pressure reach the low pressure stage.

A similar principle is applied to oil diffusion pumps constructed with metal (Fig. 5.31). The boiler is seen to be single, but the vapour rises to each of the diffusion stages by three distinct and concentric pipes dipping into oil at their lower end. The central tube corresponds to the diffusion stage located on the side of the high vacuum. After condensation, the result is that oil firstly passes through the external area of the boiler and only the products having the lower vapour pressure reach the middle part.

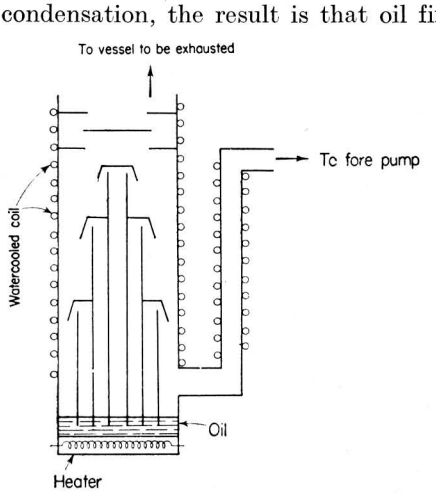


FIG. 5.31

In modern pumps, the cooling required for condensation is obtained with the help of a tubular copper coil soldered to the external wall of the pump. This coil is traversed by a water flow.

Cooling is also provided on the circuit of the fore-vacuum in order to condense oil vapours which might be driven out.

These pumps are now commonly constructed in types whose speeds measured at 10^{-4} mm Hg, lie between 10 l./sec and 20,000 l./sec. Their limiting vacuum, depending on the oils used is about 10^{-6} to 10^{-7} mm Hg. The power of the electric heater is 100 W for the

smallest ones, and 6 kW for the biggest ones. The water flow required for the cooling goes from 0·3 to 10 l./min, and the quantity of oil they contain from 10 cm³ to 3 l.

Their weight lies between 3 and 300 kg, their height from 30 to 2000 cm, their diameter from 6 to 80 cm. Lastly, it must be pointed out that these pumps require to be backed by fore-pressures below 1 mm Hg, generally of the order of 0·1 mm.

Their speed is nearly constant between 10^{-3} and 10^{-5} mm Hg. Figure 5.32 represents a typical curve.

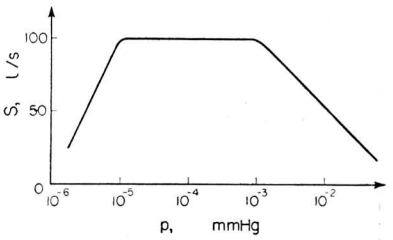


FIG. 5.32

5.1.3.4. *The Ionization Pump*

The essential principle of the ionization pump is the following: if the gas of a vessel to be exhausted is ionized, the molecules are apt to be directed into an electric field, and the latter may be set so that ions are led to the fore-vacuum prepared by a backing-pump.

For a long time, it has been observed that the pressure in a discharge tube decreases with time, because the ions reaching the electrodes with a high speed are fixed by adsorption (see Sec. 4.3.4). This is not a true pumping effect, because such a system stops working when the electrodes are saturated with gas.

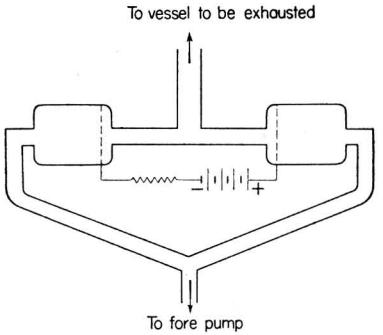


FIG. 5.33

The first experimental ionization pump was constructed in 1950.†

It consisted of a glass tube connected at its centre to the vessel to be exhausted (Fig. 5.33). On each side, the tube contained a grid between which a potential difference of about 1000 V was applied, in order to bring about a discharge. According to their sign, the ions were led to one or the other grid, where they lost their charge, and from there they were removed by the fore-pump. This rather rudimentary device

† R. Champeix, *Compt. rend. acad. sci.*, 3 juillet 1950.

has been improved by the Compagnie Générale de T. S. F., France, which used, as proposed by R. Champeix, a thermionic filament emitting electrons required to ionize the gas; and in addition, inside the pump, an electron-optical system focused the ions produced on the exhaust orifice. Then, a pumping-speed of 18 l./sec was obtained.

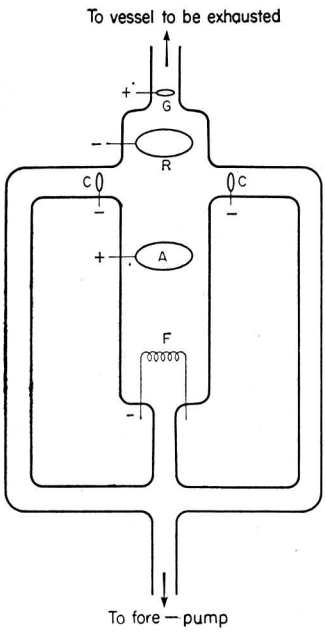


FIG. 5.34

On his side H. Schwarz† has built up an ion-pump the diagram of which is represented in Fig. 5.34.

Ionizing electrons are emitted by a tungsten filament F and are attracted by an anode. A repulsion electrode R, combined with an axial magnetic field, forces the ions to make a series of oscillations and give them helical paths, which very much increases their ionization probabilities.

The emitted ions are led to the fore-vacuum thanks to the rings C, while the ring G prevents them from going back to the vessel to be exhausted.

Schwarz claims a pumping speed of some l./sec between 10^{-3} and 10^{-5} mm Hg, with a limiting pressure of about 10^{-6} mm Hg.

5.1.3.5. *The Absorption Pump*

In December 1954, Davis and Divotia described‡ a pump of a new kind, utilizing the phenomenon of continuous absorption of gases by a continuously evaporated metal; evidently there is a close relationship between the working of this pump and the working of "getters", the mechanism of which will be studied at the end of this chapter.

The Davis and Divotia pump (Fig. 5.35) employs evaporation of a titanium wire continuously unrolling from a spool moved by a little motor.

Titanium comes into contact with a graphite crucible at red heat by bombardment of electrons issuing from an incandescent tungsten

† H. Schwarz, *Le Vide*, No. **42**, p. 1263, 1952.
‡ *Rev. Sci. Instr.* **25**, 12, p. 1193, 1954.

filament. Titanium vapour is condensed on the pump walls, strongly absorbing gases.

This absorption is made still stronger by using a part of the electrons emitted by the incandescent filament to ionize molecules. Owing to an electric field created by a system of grids, they are then obliged to move to the walls on which they are fixed and absorbed by the titanium coating.

The authors say that with a consumption of 7 mg of titanium per min and with a total electric power of 1 kW, they have obtained a pumping speed of 5 to 6000 l./sec for hydrogen under a few units of 10^{-6} mm Hg, and a limiting vacuum of about 2×10^{-7} mm Hg.

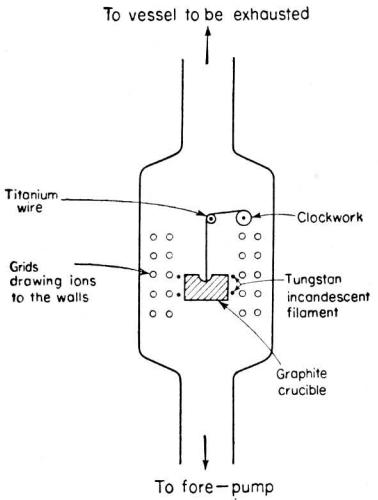


FIG. 5.35a. Schematic diagram of the Davis and Divotia's absorption pump

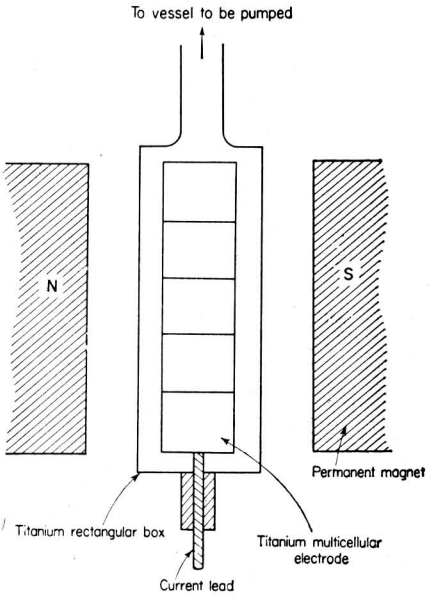


FIG. 5.35b. Schematic diagram of the Varian VacIon pump

At the present time, several manufacturers have marketed various absorption pumps. For example, we shall describe the VARIAN pump and the C. S. F. one.

1. The VARIAN VacIon pump has a structure rather similar to that of the PENNING gauge (see Sec. 6.5.2). It includes the following parts (Fig. 5.35b):

(a) An air-tight box, the walls of which are made of titanium. This box is connected to the negative pole of a voltage source.

(b) A multicellular electrode also made of titanium, the axis of each cell being normal to the box sides. It constitutes the anode and is connected to the positive pole of the source.

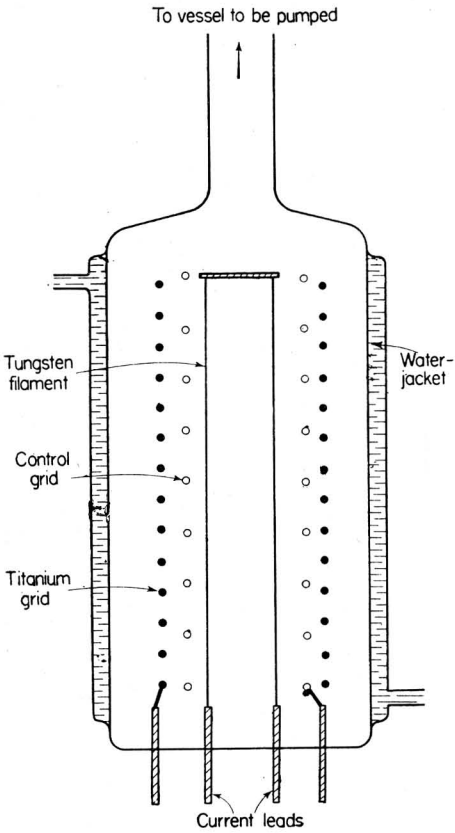


FIG. 5.35c. Schematic diagram of the C. S. F. titanium pump

(c) A permanent magnet producing a field of about 500G parallel to the axis of the cells.

This device operates quite like the PENNING gauge: (see Sec. 6.5.2) after a fore-vacuum has been made with a vane-type pump, a voltage of 2000 V is applied between the electrodes, and a cold discharge takes place. The electrons running towards the anode as well as the ions flowing to the cathode move along helical paths, which widely increases their travel and consequently the collision probability. The ions are stuck on the walls by titanium.

This pump has the following performances:

Fore-pressure: $< 0{\cdot}1$ mm Hg;

Limiting pressure: $\approx 10^{-7}$ mm Hg;

Pumping speed for air at 10^{-6} mm Hg: ≈ 10 l./sec;

Power consumption at 10^{-1} mm Hg: 1000 W;

Power consumption at 10^{-4} mm Hg and below: 100 W.

Besides, the current which passes through the pump is closely related to the pressure, which allows to do without a gauge.

2. The C. S. F.† pump has a structure which is like the one of the hot-cathode ionization gauge (see Sec. 6.5.3).

† C. S. F.: Compagnie Générale de Télégraphie Sans Fil, Paris, France.

Electrons are emitted by a hot tungsten filament (Fig. 5.35c) They pass through a control grid and come to strike a second grid which is covered with a thick titanium layer. Owing to the temperature rise due to electron bombardment, titanium evaporates and deposits on the water-cooled walls of the pump. Then,the ions produced by the collisions of electrons on molecules are driven towards the walls where they are absorbed by titanium.

The characteristics of this pump are as follows:

Fore-vacuum: 10^{-3} mm Hg; Limiting pressure: 10^{-9} mm Hg;

Pumping speed for air at 10^{-6} mm Hg: 18 l./sec;

Power consumption at 10^{-3} mm Hg: 800 W;

Power consumption at 10^{-6} mm Hg and below: 600 W.

This pump is particularly useful for very high vacuum devices (see Sec. 7.5).

5.2. GETTERS

It has been seen above that it is nearly impossible to degas metals and glass entirely. Then it must be expected that, in a vessel in which the pressure has been decreased to a certain value, this pressure rises more or less quickly with time, owing to the fact that the walls and the parts contained in it evolve some gas.

Besides, in mass production, the demands of the cost price prevent one from exhausting and ovening electron tubes as long as it should be necessary to degas them completely.

On the other hand, because of the complexity of using liquid-air traps for mass production, it is not possible to pump high quantities of tubes by using these traps. Consequently, a residual vapour pressure of the pumping fluid will remain in these tubes.

Even in the case in which fluids with a low limiting vacuum are used (oil diffusion pumps), it is not always possible to take advantage of it because of the small diameter of the exhaust pipes (stems): lack of time.

For all these reasons, getters are used. They are substances, generally metals, which, inserted into the bulb of an electron tube, have the effects of:

(a) improving the vacuum supplied by the pump;

(b) absorbing the gases evolved during the life of the tube.

According as to whether volatile bodies are concerned which are made to distil during or after pumping, or on the contrary, whether bodies are concerned which are not evaporated, getters are divided into:

(a) volatilized getters;

(b) non-volatilized getters.

5.2.1. Volatilized getters

These getters are made of a small quantity of an easily volatile metal, put on a small metal plate which is heated during or after pumping, so that the metal is evaporated and deposits on the bulb making a more or less bright spot, called a "mirror".

These are almost the only getters used in small receiving tubes.

5.2.1.1. *Conditions Required from Volatilized Getters*

They must fulfil the following demands:†

(a) A low vapour pressure ($p_0 < 10^{-4}$ mm) at the baking temperature ($T = 400°C$).

(b) A vapour pressure high enough at the temperature at which their base plate is heated ($p_0 > 1$ mm at about 600–1000°C).

(c) A negligible vapour pressure ($p_0 \ll 10^{-6}$ mm Hg) at the temperature of the normal working of the bulb on which they are deposited.

(d) A high gas absorption efficiency, particularly of oxygen, at temperatures lying between 20 and 200°C (temperatures of the bulb during a normal working of the electron tube). Especially the compounds resulting from the effect of gases upon the getter (oxides, for instance) must not make an impenetrable layer on the surface of the "mirror". Gases must be able to enter the mass itself of the metal coating.

(e) The chemical compounds of the gases and of the metal must not be split, while working, under the action of heat or of bombardment by parasitic electrons.

5.2.1.2. *Metals Used as Volatilized Getters*

Experiment shows a small number of metals fulfil these various demands.

† Espe and Knoll, *Electronics*, October, 1950.

Aluminium acts only with oxygen and gets covered with an alumina skin, which is impenetrable later on. Besides it is difficult to evaporate.

Magnesium is very active towards oxygen, but inversely to aluminium, it evaporates too easily, so that with power tubes the danger of migration of magnesium may occur during working. It was very much used with the first "low heating consumption" radio tubes, using thoriated tungsten filaments (about 1925). Just as aluminium, magnesium has the disadvantage of becoming covered with an impenetrable oxide layer. In modern tubes, magnesium is used:

As an additional getter, in the form of a particle of about 1 mm^3, which is fixed on one of the grid rods, and which is evaporated by electron bombardment during the activation following the pumping (Fig. 5.36) (see Vol. II, Sec. 14.5).

As a getter in mercury-vapour rectifiers and thyratrons, because it does not absorb this vapour.

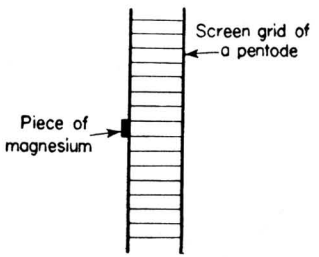


FIG. 5.36

As a general rule, alkaline-earth metals are very good getters to be volatilized.

In practice, *barium* is mostly used, because in tubes using oxide-coated cathodes, it has the advantage, if it accidentally deposits on the cathode, of not poisoning the latter, and even sometimes of improving its electron emission.

Barium fulfils all the conditions listed in Sec. 5.2.1.1. However, barium being strongly oxidizable and hydratable when exposed to air, it has been necessary to use artificial means to employ it:

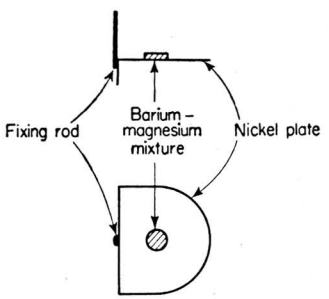


FIG. 5.37

(a) Firstly have been used (and sometimes are still used) pastilles of 20 to 50 mg of an alloy containing 25% Ba and 75% Mg. Magnesium protects barium from oxidizing† (Fig. 5.37).

(b) Pure barium protected by a nickel tube is now mostly used (Ba–Ni). The barium powder is inserted in a rather short (30 cm)

† This alloy is known under the trade-name of Kemet.

nickel tube with a large diameter (1 cm) in a neutral atmosphere. Then, after plugging, the tube is stretched down to a diameter of 1 to 2 mm. Thus is obtained a nickel wire with a barium core (Fig. 5.38).

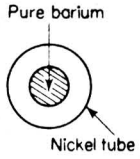


FIG. 5.38

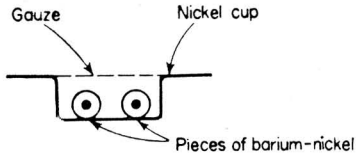
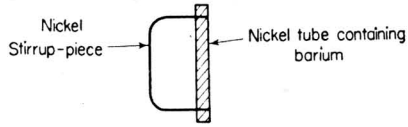


FIG. 5.39

To use it, some pieces of 4 to 5 mm are cut with snips, and they are placed in small nickel caps where they are maintained by a gauze (Fig. 5.39). The cutting must crush the ends of the nickel tube to protect barium. Anyway, it is advisable to use the cut pieces in the following hour.



KIC getter is a variant: the nickel tube containing barium has been previously ground to make the wall thinner along a generatrix. This tube is welded to a stirrup, so that its ends are tightly closed by the welding; this allows one to keep these getters a long time in air before using them. By heating the resulting ring, the pressure of barium vapour makes the thin wall burst (Fig. 5.40).

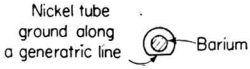


FIG. 5.40

The great efficiency of *calcium* must be mentioned. It was commonly used around 1930, and it should merit being used again.

5.2.1.3. *How to Use Volatilized Getters*

The getter is inserted in the bulb at such a point that the evaporated metal deposits on the glass wall, exclusive of any other place where it could bring about noxious effects, such as electric leakages, short circuits, dielectric losses, etc.

Evaporation ("flash") of the getter is often produced for reasons of convenience and automation, on the pump itself, just before the sealing of the pumping stem.

When the appropriate moment comes, a coil supplied with high-frequency current is brought near to the getter. The field produced

by this coil is frequently strengthened by a magnetic ferrite core. The getter plate is then made red hot and the getter metal evaporates (Fig. 5.41) (see also Sec. 8.4.2.2).

Because of the small diameter of the stem required for ease of sealing, the pressure has no time to rise in the bulb between the flashing and the sealing-time. In fact, the getter efficiency is often observed to be better when it is evaporated after the sealing.

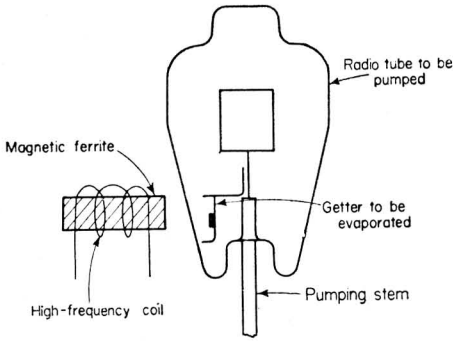


FIG. 5.41

In some cases, it is impossible to heat the getter by high frequency. Then a tantalum wire coated with barium oxide (Batalum) may be heated by Joule effect. Tantalum reduces the oxide and barium is released.

5.2.2. **Non-volatilized getters**

Very often it is not advisable nor possible to volatilize in a tube metallic vapours (electric leakages, contaminations, etc.).

It is then desirable to absorb the gases with the help of a non-evaporated product.

(a) The first getter chronologically which has been used, was of that type: it was *phosphorus* which was used in vacuum incandescent-light-lamps of the type known as "monowatt" (1 W per candle). By dipping in white phosphorus dissolved in carbon disulphide, the central glass bar bearing the filament becomes coated with phosphorus. The latter absorbs oxygen especially, which increases the life of the lamps; this is an out-of-date system, because of the better quality of vacuum obtained with modern pumps.

(b) *Tantalum* sheets were used for a long time, from 1930 to 1940, to make the anodes of transmitting tubes for a few kilowatts. When it is kept at about 1000°C by electron bombardment, tantalum behaves as an excellent getter.

(c) Now *zirconium* is used in special electron tubes; it acts only when it is heated to about 400–500°C. For that reason, it is put on the anode of small transmitting tubes, in the form of powder in sus-

pension in an organic solvent. Then these coated parts are heated at 800°C in vacuum, which gives a good adhesion of zirconium. At the same time, the superficial layer of the treated surface becomes greyish and acquires a high total emissivity. During working, the anode is heated by electron bombardment to the required temperature.†

(d) Ceto-getter (alloy of *cerium* and *thorium*) is a recent type of non-volatilized cold-working getter. In suspension in an organic solvent, the powder is brush-painted on the anode of certain sub-miniature tubes, in which it is impossible to set a normal getter, because it is too bulky.

(e) The high possibilities of gas absorption by *titanium* allow one to foresee new applications of this metal as a getter. One of these has already been seen in the evaporation pump. On the other hand, its sealing properties with special ceramics are already used to make electron tubes for high frequencies constructed with alternate series of ceramic cylinders and titanium discs used as "current leads" (see Vol. II, Sec. 9.2). Moreover, the presence inside the vacuum chamber of these titanium absorbing parts allows the pumping requirements to be greatly reduced.

† The absorption process of gases by zirconium and titanium is rather complex. As is shown by the curves of Fig. 4.10, this adsorption is the higher, the lower the temperature. However, to absorb, *the metal first must be very highly heated*: *when it is cooling down, then absorption occurs.* Desorption then occurs only when the metal is heated at a temperature higher than the initial temperature. Experimentally, it is ascertained that it is better to give to the getter metal a temperature gradient so that the different gases may be absorbed at the points of optimum temperature: for example, one end of a piece of a titanium ribbon may be welded to the cathode, the other end remaining free.

CHAPTER VI

MEASUREMENT OF LOW PRESSURES

CLASSIFICATION OF MANOMETERS

1. Manometers using the mechanical effects of pressure
   (a) Manometers using the deformation of a reservoir
   (b) Manometers using a change in level of a liquid
2. Manometers applying Boyle's law
   (a) The McLeod gauge and its variants
   (b) The Dubrovine gauge
3. Manometers applying laws of kinetic theory
   (a) The Knudsen radiometric-manometer
   (b) The Dushman viscosity-manometer
4. Manometers using thermal convection phenomena
   (a) The Pirani Gauge
   (b) The thermocouple gauge
5. Manometers using ionization phenomena
   (a) The discharge tube
   (b) The cold-cathode ionization gauge (Penning or Philips gauge)
   (c) The hot-cathode gauge
   (d) The radioactivity gauge (alphatron)

6.1. MANOMETERS USING MECHANICAL EFFECTS OF PRESSURE

6.1.1. Manometers using the deformation of a reservoir

These classical devices will be mentioned only as a reminder (Figs. 6.1 and 6.2).

Measurement range: 1 cm – 76 cm Hg and above;
Advantages: plainness and strength;
Disadvantages: low sensitivity, accuracy and fidelity.

6.1.2. Manometers using a change in level of a liquid

A barometric tube may be used for pressure measurement between 1 and 760 mm, on condition that it is accompanied by a pilot-barometer giving at any moment the atmospheric pressure. The pressure in the

vacuum circuit is given by the difference in level h between A and B: if mercury is the liquid used, the pressure is directly obtained in mm Hg (Fig. 6.3).

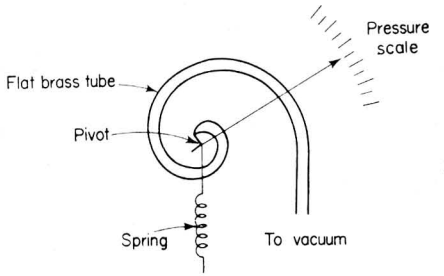


FIG. 6.1

When it is not necessary to measure more than a few dm of level difference, a U-shaped manometer may be used; it is independent of atmospheric pressure (Fig. 6.4). By inclining one of the arms, the sensitivity is multiplied by $1/\sin\theta$ (Fig. 6.5).

Lastly, taking a liquid less dense than mercury, the sensitivity is multiplied by the ratio of the densities, by 15 for instance with oil.

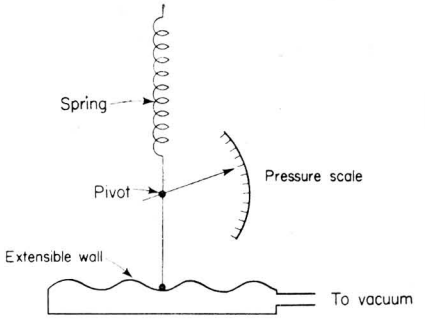


FIG. 6.2

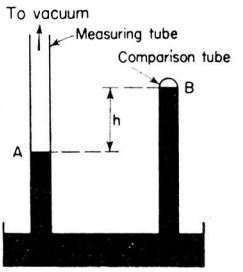


FIG. 6.3

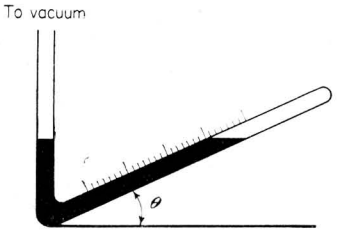


FIG. 6.4

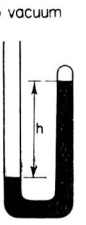


FIG. 6.5

These manometers offer the advantage of being easily constructed, of allowing continuous readings and of having a satisfactory accuracy.

6.2. MANOMETERS USING BOYLE'S LAW

6.2.1. The McLeod gauge

This gauge has a special interest because it is often used as a standard gauge.

6.2.1.1. *Principle*

It comprises (Fig. 6.6):

A reservoir R containing some mercury, which can be raised or lowered by hand or by any other procedure.

A bulb V, topped by a fine tube T (compression tube) and connected to both the reservoir R and the vacuum system.

At rest, the vessel R must be set low enough for mercury to fall by gravity down to the level A, then connecting V to the system.

To make a measurement, R is raised so that mercury climbs the right hand tube (called the comparison tube) up to a certain level C. In the tube T (the compression tube), mercury compresses a certain quantity of gas and goes up to a level B lower than C. Calling V the initial volume of the isolated gas measured under the pressure p, and v the final volume under the pressure p_1, it is obtained that:

$$p = p_1 \frac{v}{V} . \qquad (6.1)$$

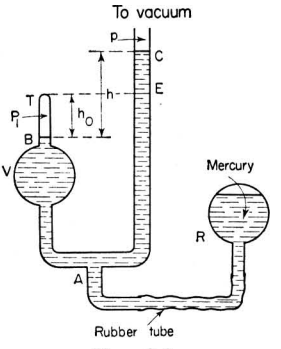


FIG. 6.6

If p and p_1 are expressed in mm Hg, h being the difference in level of mercury in both tubes, consequently it follows that:

$$h = p_1 - p \text{ and } p_1 = h + p \qquad (6.2)$$

whence:

$$p = (h + p) \frac{v}{V} . \qquad (6.3)$$

This is usually simplified, as $p \ll h$:

$$p = h \frac{v}{V} , \qquad (6.4)$$

v and V being given by the construction, the value of p is then deduced. (v/V is the *compression factor* of the gauge.)

6.2.1.2. *Calibration*

This gauge may be calibrated in two different ways:

(a) *Linear calibration.* For that, it is prescribed to lift mercury to a mark B on the compression tube at a distance h_0 from the top. In the comparison tube, mercury goes up to h (mark C). There is then obtained calling d the diameter of the tube T:

$$p = \frac{v}{V} h = \frac{\pi d^2}{4 V} h_0 h = c_1 h. \tag{6.5}$$

The quantity:

$$c_1 = \frac{\pi d^2}{4 V} h_0 \tag{6.6}$$

is the constant of the gauge for a linear calibration.

(b) *Quadratic calibration.* This time, the mercury is lifted to a mark E on the comparison tube at the level of the top of the compression tube. The mercury then rises through the latter to a point at a new distance h from the top (not mentioned on the figure).

Then there is obtained:

$$p = \frac{v}{V} h = \frac{\pi d^2}{4 V} h \times h = c_2 h^2. \tag{6.7}$$

The quantity:

$$c_2 = \frac{\pi d^2}{4 V} \tag{6.8}$$

is the constant of the gauge for a quadratic calibration.

6.2.1.3. *Some Details about the Construction*

Mercury shifting. Raising and lowering of the mercury may be produced in two different ways:

Either manually, the mercury reservoir being connected to the gauge with a rubber pipe, as above;

or by fixing the mercury reservoir, and by connecting it, thanks to a two-way tap, either to the atmosphere (for raising) or to the vacuum-system (for lowering) (Fig. 6.7).

Compensation of capillarity phenomena. The compression and comparison tubes must have the same diameter in order to avoid errors due to the differences of capillarity. Now, the compression tube has, as will be seen later on, a small diameter (about 1 mm). With

such a diameter, the conductance of the comparison tube (see Sec. 7.1), would be low, and the pressure equilibrium between the volume V and the vacuum system would require too much time. To remedy this difficulty, a rather large diameter (1 to 2 cm) is given to the tube connecting the gauge to the vacuum system, and there is then attached a side derivation circuit made of a tube having the same diameter as the compression tube: it is this fine tube which is used to compare the levels of the mercury (Fig. 6.8).

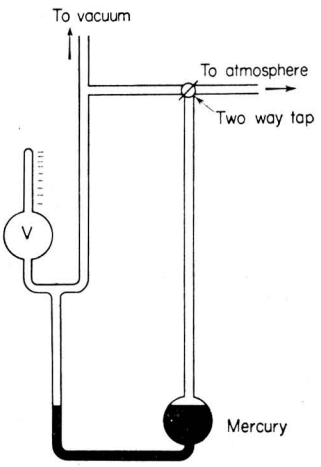


FIG. 6.7

L. Dunoyer's gauge with various sensitivity ranges. Instead of using one single compression tube, if several superposed tubes with decreasing diameters are used, several sensitivity ranges are obtained and so the accuracy of the gauge is improved (Fig. 6.9).

Upper sensitivity of a McLeod gauge. From the above formulae, it is seen that to have a sensitive gauge (p small), d must be decreased and V raised.

Concerning d, it is not possible to decrease it below 0·8 mm, because mercury would stick to glass. On the other hand, it is not possible for V to be greater than 250 cm³ (which already corresponds to a weight of mercury of 3·4 kg), because the gauge would require a special construction to bear this weight. In these conditions, if $h = 1$ mm, it is found:

$$p \approx 10^{-6} \text{ mm Hg}.$$

That is about the lowest pressure which can be measured with a practically constructed McLeod gauge. It is to be noticed that with so low a pressure, an error of reading on h involves a large uncertainty of p.

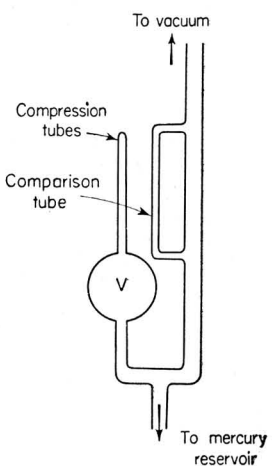


FIG. 6.8

Advantages and disadvantages of the McLeod gauge. One of the chief qualities of a McLeod

gauge is that it may be completely calculated, which allows it to be used as a standard gauge.

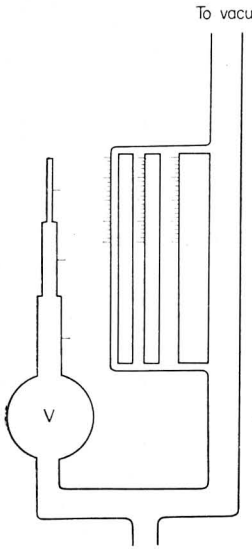


FIG. 6.9

On the other hand, it suffers from various disadvantages:

Each measurement requires an operation: the gauge does not give continuous reading.

Because of the high compression coefficient to which the gas is subjected (of about 10^4 to 10^6), the easily condensed gases (H_2O, CO_2...) are reduced to liquid state and their partial pressure is not measured. It is the same for the mercury vapour brought by the gauge itself, the presence of which is not indicated during a measurement. Consequently, when it is required to measure some pressures lower than 10^{-3} mm Hg (pressure of mercury vapour at 20°C), it is compulsory to set between the gauge and the vacuum system a freezing-trap to prevent mercury vapour from passing over the system.

6.2.2. **The Dubrovine gauge**

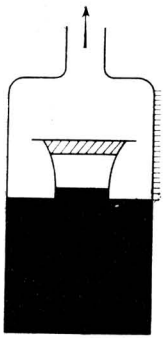


FIG. 6.10

In its plainer form, it is a test-tube containing a little air, turned over the mercury contained in a bottle connected to the vacuum system. When a vacuum is obtained, the test-tube rises. Its equilibrium results from a compromise between gravity, Archimedes' thrust and gas expansion (Fig. 6.10).

Thus, pressures lying between 0·1 and 10 mm Hg may be measured by continuous readings.

6.3. MANOMETERS USING THE LAWS OF KINETIC THEORY

Generally, these manometers bring into play the energy of the thermal agitation of the whole of the gas molecules; this energy depends on the pressure.

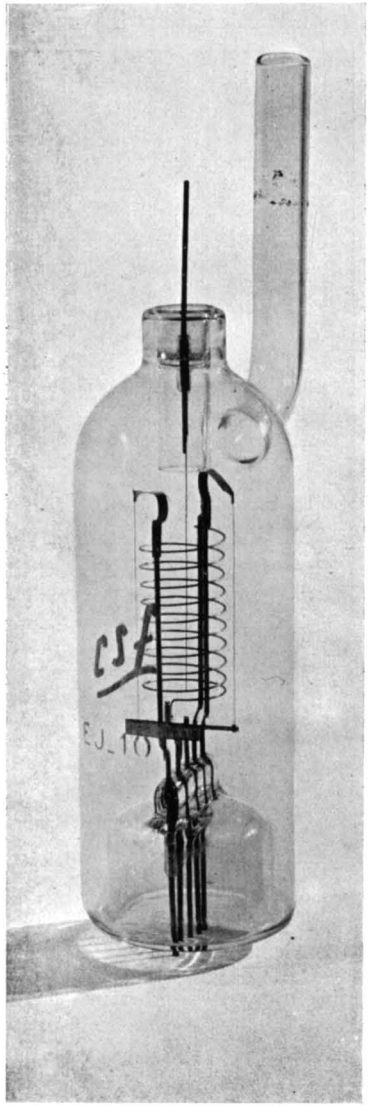
6.3.1. The Knudsen molecular or radiometric manometer

6.3.1.1. *Principle*

Consider two flat and parallel plates A and B set in a vessel containing a rarefied gas under the pressure p and at the temperature T

Plate 3. A dismantled oil diffusion pump, stainless steel construction. At left, the three-stage diffusion nozzle
(Courtesy "Laboratoire des Basses Pressions", Argenteuil, France)

(a)



(b)

Plate 4.

(a) The C. S. F. titanium pump

(b) A Bayard-Alpert type ionization gauge

(Courtesy "Compagnie Générale de Télégraphie Sans Fil" Paris, France)

(Fig. 6.11). If these plates have the same temperature T as the other parts of the chamber, because of reasons of symmetry, no resulting force is exerted upon the plates.

On the contrary, if one of the plates has a temperature different from T, these plates are attracted if $T_1 < T$ and are repelled if $T_1 > T$. It is easier always to use this last case.

The repulsing (or the attracting) forces are shown to be proportional to the pressure, which allows a manometer to be constructed.

The method of reasoning will be the same as for thermal effusion (Chap. II, Sec. 2.2.11).

The number of collisions on a wall, per second and per square centimetre is:

$$n_t = \frac{1}{4} n v_m. \tag{2.54}$$

Taking into account that the pressure, in the neighbourhood of the plate A (at the temperature T), is that prevailing in the vessel, namely p, the number of collisions per second and per square centimetre on this plate is:

$$n_t = \frac{1}{4} \frac{p}{k T} \sqrt{\left(\frac{8 k T}{\pi m}\right)}. \tag{6.9}$$

On the other hand, in the neighbourhood of the plate B (at the temperature T_1) the pressure is p_1. The number of collisions per second and per square centimetre on this plate is:

$$n_t' = \frac{1}{4} \frac{p_1}{k T_1} \sqrt{\left(\frac{8 k T_1}{\pi m}\right)}. \tag{6.10}$$

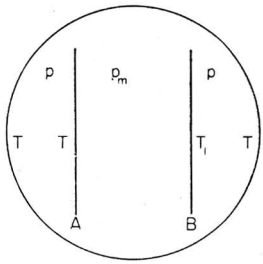


FIG. 6.11

For a reason of symmetry, n_t must be equal to n_t', which gives:

$$\frac{p}{p_1} = \sqrt{\frac{T}{T_1}}. \tag{6.11}$$

Suppose the plate B to be fixed and the plate A movable, and let S be their common surface. The plate A suffers, because of the mean pressure p_m prevailing between the two plates ($p_m = (p + p_1)/2$) a force equal to $S \times p_m$, and because of the external pressure p, a force equal to $S \times p$.

The resulting force is then:

$$F = S\,(p_m - p) = S\left[\frac{p_1 - p}{2}\right] \tag{6.12}$$

or, after eq. (6.11):

$$F = \frac{S\,p}{2}\left[\sqrt{\left(\frac{T_1}{T}\right)} - 1\right]. \tag{6.13}$$

Now, let us provide the movable plate with a return spring and with a needle moving on a calibrated scale.

Thus, a manometer has been devised which offers the following characteristics:

(a) The force tending to deviate the movable plate from the fixed one is proportional to the pressure p in the chamber.

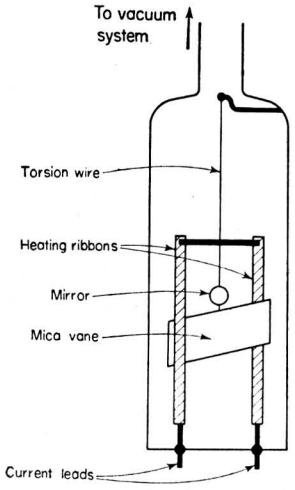


FIG. 6.12

(b) This is true on the condition that the collisions of molecules against the plates are dominating the collisions of molecules amongst themselves; therefore this device works only in the molecular region.

(c) The higher $\sqrt{(T_1/T)}$, the higher is this force.

(d) This force depends neither on the nature of the gas, nor on the shape or the distance between the electrodes, but only on their common surface.

6.3.1.2. *Construction of the Knudsen Manometer*

Figure 6.12 represents a simple arrangement of this apparatus: a rectangular mica-vane of 20 μ thickness is suspended by a torsion wire.

At both sides of this vane, two nickel-chromium ribbons are set, which are heated by the Joule effect.

The rotation of the rectangular mica-sheet under the molecule impact is recorded thanks to a small mirror, by the Poggendorff's method.

The Knudsen gauge allows us to measure easily pressures of about 10^{-7} mm Hg. With improved apparatus, one may go down to about 10^{-9}.

Figure 6.13 shows a typical calibration curve for such a gauge. It is seen that the mirror deflexion is proportional to the pressure only when the latter is low: the mean free path must be high compared with the distance from

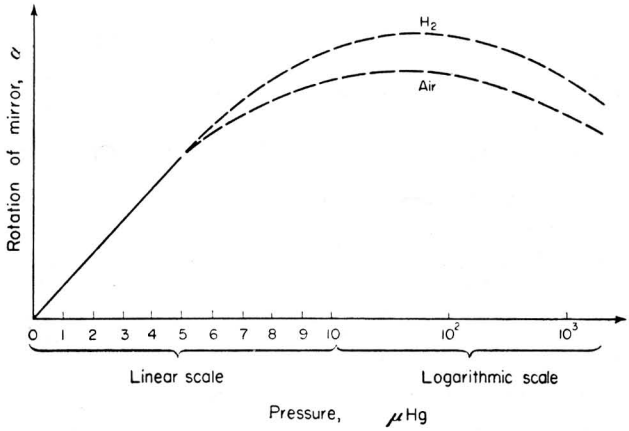


FIG. 6.13

the movable vane to the hot ribbons. For high pressures the deflexion is no longer independent of the nature of the gas, as viscosity interferes.

6.3.1.3. *Advantages and disadvantages of the Knudsen manometer*

(a) *Advantages*: high sensitivity, good fidelity, independence with respect to the nature of gas, possibility of realizing an absolute manometer.

(b) *Disadvantages*: fragility and inconvenience of use due to the moving part. This is the reason why this gauge is hardly used outside laboratories.

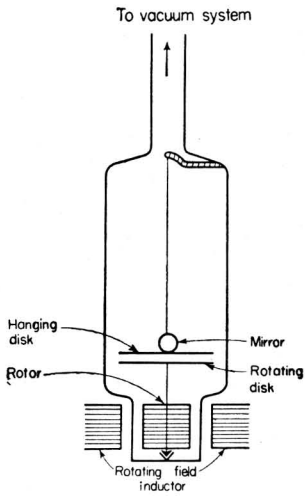


FIG. 6.14

6.3.2. **The Dushman viscosity manometer**

Let us refer to the experiment of Fig. 2.15 and to the curve of Fig. 2.22. When the pressure is low enough for the mean free path to be greater than the distance between the two disks, proportionality exists between the pressure and the deflexion of the suspended disk.

Figure 6.14 shows how Dushman used this phenomenon to realize a vacuum gauge. The rotation of the lower disk is obtained thanks to a rotary induction field set in air and acting upon the rotor through the bulb.

This apparatus allows us to work down to about 10^{-7} mm Hg.

As for the Knudsen gauge, it suffers from fragility added to trouble due to vibrations brought about by the motor.

6.4. MANOMETERS USING THERMAL CONVECTION PHENOMENA

It has been seen (Chap. II, Sec. 2.3.2) that the thermal conductivity of gases for viscous flow is independent of pressure, according to the formula:

$$\lambda = \eta c_v \tag{6.14}$$

in which:

λ is the thermal conductivity coefficient;

η is the viscosity coefficient;

c_v is the specific heat at constant volume.

However, it has also been seen that for a molecular flow, the viscosity coefficient decreases with pressure, so that, for the moment, as a first approximation, λ may be written as:

$$\lambda = k p.$$

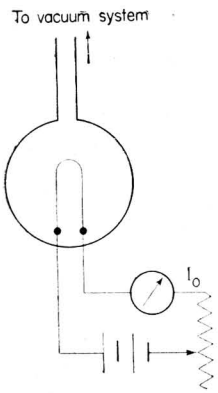


FIG. 6.15

Then, if a filament is heated with a constant power by an electric current, it will be more or less cooled down depending on the pressure of the gas in which it is located, and its temperature may be related to the pressure.

6.4.1. **The Pirani gauge**

6.4.1.1. *Principle and Construction*

In this gauge, invented in 1906, *a metal with a high temperature coefficient is used for the filament*, so that any variation of temperature produces a variation of the heating current. The latter will give a measurement of the pressure, from a previous calibration.

A particularly simple diagram is seen in Fig. 6.15. The filament is heated to a certain temperature, due to the current I_0, the vacuum

being supposed as good as possible. As soon as a gas enters the bulb, the gas cools the filament whose resistance decreases, and current rises.

Such as it is, this system suffers from the two following disadvantages:

(a) the calibration is greatly influenced by the changes of the room temperature.

(b) An important part of the ammeter scale is used for the measurement of the starting current I_0, and consequently cannot be used for the measurement of the pressure: hence a loss of sensitivity.

It is this reason why very often the device of Fig. 6.16 is more suitable because it avoids these two disadvantages. Two bulbs containing similar filaments are set in a Wheatstone-bridge arrangement (one bulb is sealed under a constant pressure, and the other one is connected to the vacuum system, the pressure of which is to be measured). A potentiometer allows one to get the bridge balance.

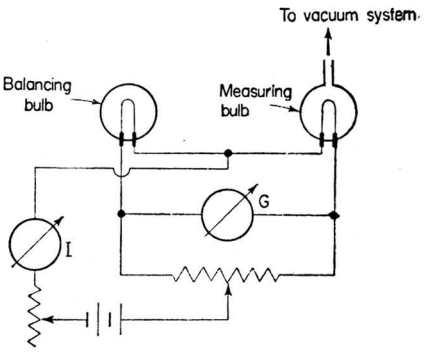


FIG. 6.16

The supply current of the bridge is adjustable, which enables the measurement range to be changed. In fact, the filaments will be heated to a higher temperature as the pressure to be measured is lower.

The metal composing the filaments must fulfil the three following conditions:

(a) To have a high temperature coefficient, which eliminates alloys such as constantan, nichrome, etc.

(b) To have a high melting-point ($>$ 1500°C).

(c) To have when heated, a good resistance to oxidation.

In practice, *platinum* best fulfils these three conditions.

6.4.1.2. *Using a Pirani Gauge*

The Pirani Gauge may be used:

(a) Either by operating the potentiometer-cursor so that at any value of the pressure the bridge is balanced. The position of the cursor is

then calibrated in pressure units. This method is accurate, but requires an operation for each reading.

(b) Or, by fixing the cursor and measuring the pressure from the deflexion of the galvanometer G. This procedure avoids the above disadvantage and enables one to make remote measurements, by transmitting the galvanometer current.

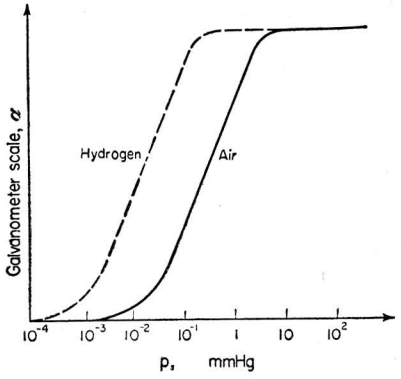


FIG. 6.17

What is the measurement range of a Pirani gauge? The thermal conductivity of a gas is known to be independent of pressure in the viscous state. Thus from 760 mm to about 10 mm, the gauge will be unusable.

On the other hand, below 10^{-3} mm, the heat losses of the filament by radiation and by conductivity prevail very much over the convection cooling.

Then, in practice, the Pirani gauge works best between 10 mm Hg and 10^{-3} mm Hg.†

The calibration of the Pirani gauge depends on the nature of gases, as they have not all the same thermal conductivity coefficient: for instance, hydrogen being a better heat conductor than air, it will give a calibration curve displaced to low pressures (Fig. 6.17).

6.4.2. **The thermocouple gauge**

In the Pirani gauge, the temperature variations of the filament are measured by the variations of its resistance. In the thermocouple gauge, the temperature variations are recorded by the variations of the thermoelectric e.m.f. of a couple of two appropriate metals, the junction of which is in contact with the filament.

The filament F is supplied by a battery, a rheostat and an ammeter, which, by regulating the heating current, makes possible the variation of the sensitivity range of the apparatus. The metals M_1 and M_2 of the thermocouple (rhodiated platinum to platinum, or else chromel to alumel) are connected to a galvanometer graduated in pressure units (Fig. 6.18).

† L. Dunoyer has made a careful study of the Pirani gauge: *Le Vide*, 1949, Nos. **20**, **21**, **22**, **23**.

The range of working is the same as the Pirani gauge (10^{-3} to 10 mm Hg), but the sensitivity is less, because a bridge-arrangement is not used.†

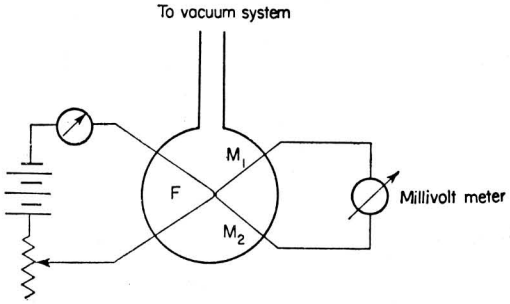


FIG. 6.18

6.5. IONIZATION MANOMETERS

The general principle of these manometers is the aim to produce an ionization in the gas whose pressure is to be measured, and to measure the quantity of ions produced, a quantity evidently rising, in a certain range, in terms of pressure.

6.5.1. **The discharge tube**

This device gives only rough information about pressure, but it is extremely useful because of its plainness and the quickness of its recordings.

It is composed of a glass tube containing two electrodes 10 to 15 cm apart, between which is applied a potential difference of some thousands of volts, obtained from a transformer or a Rhumkorff coil (Fig. 6.19).

At atmospheric pressure, the voltage is too low or the distance between the electrodes too large for the discharge to strike. That occurs from about 10 mm Hg, in the shape of a fine thread of light, located nearly on the axis of the tube.

When the pressure is reduced, the light ray becomes broader and, at about 1 mm Hg, it fills all the section of the tube: at the same time, the brightness decreases.

At about 0.1 mm Hg, the glimmer looks very pale and streaks appear, especially if d. c. current is used.

Below 0·01 mm Hg, the gas no more appreciably emits any light by itself, but the ions and electrons remaining in the discharge impinge on the glass walls and energize a greenish fluorescence.

† For more details on the thermocouple gauge, see D. Degras, *Le Vide*, March 1952, p. 1153.

Finally, at about 10^{-3} mm, all light phenomenon disappears. The discharge tube is said to be "cut-off".

The discharge tube gives some information not only about pressure, but also about the nature of the gas. Air gives a very characteristic discharge, violet-coloured for high pressures, and pinkish for low pressures. Mercury vapour gives a pale blue colour, carbon dioxide is of a darker blue and neon gives off the well-known orange-red colour, etc.

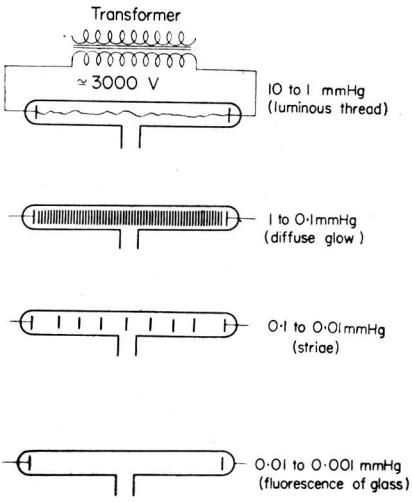


FIG. 6.19

During the pumping of an electron tube, it is possible to do without a discharge tube, by using a high-frequency high-voltage coil (Tesla coil described in Fig. 6.20). A vibrator supplied by mains energizes the oscillations of an oscillating circuit included in an insulating handle. The voltage produced is applied to a stick (antenna) fixed to this handle. It is then sufficient to bring the stick near to the glass vacuum system

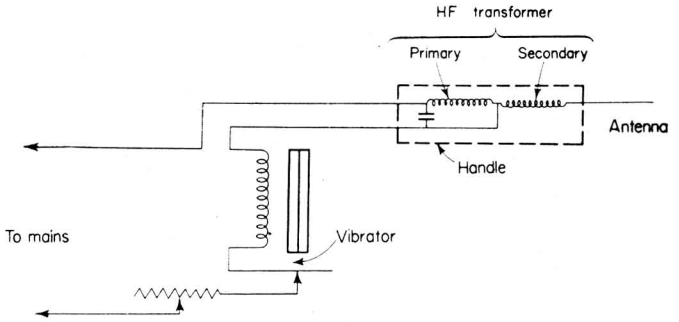


FIG. 6.20

or to the tube under pumping, for the h.f. passing by capacity to energize gas-luminescence.

In Chapter VII this apparatus will be seen to be used for leak finding.

6.5.2. The cold-cathode Penning gauge†

The discharge tube cannot give indications about pressures below 10^{-3} mm Hg, because the mean free path becomes so high that the probability of ionization is small.

Penning thought how to increase this probability very much by arranging a magnetic field parallel to the general paths of ions and electrons, so that by forcing both particles to describe helical paths, the distances travelled were greatly increased and consequently their chances of collisions.

The cathode is made of two nickel plates lying on both sides of a nickel ring used as an anode (Fig. 6.21). The circuit comprises a direct current generator of about 1000 V, a protecting resistor of 1 MΩ and a milliammeter of 1 mA.

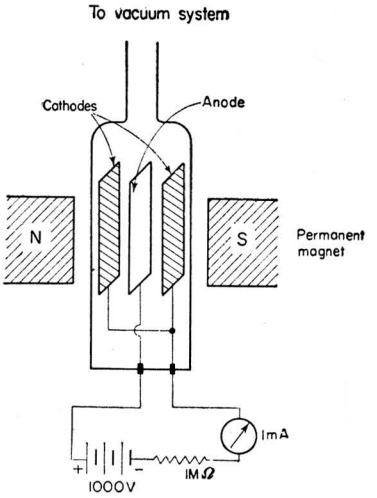


FIG. 6.21

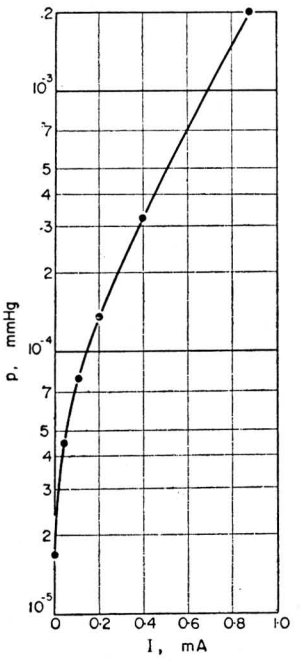


FIG. 6.22

A magnetic field of 400 oerstedts is created by a permanent magnet perpendicular to the electrode plane.

According to Penning, the increase of the path length results not only from the presence of a magnetic field, but also from a series of transverse oscillations which electrons make in the plane of the anode ring before impinging upon it.

† Or Philips gauge.

The measurement range covers from about 10^{-3} mm Hg (for $I = 1$ mA) to 10^{-5} mm Hg (for $I = 0$) (see curve Fig. 6.22).

In a later pattern, the sensitivity goes down to 10^{-7} mm Hg (with a more sensitive galvanometer) by using a closed structure and not an open one as indicated above (Fig. 6.23). The anode is then a cylinder and the cathodes are two disks nearly stopping up the ends of the cylinder.

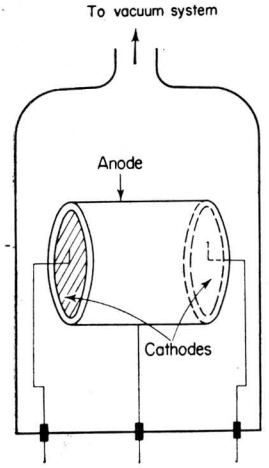


FIG. 6.23

The Penning gauge has the advantage of being very robust and practical. On the contrary it suffers from the disadvantage of lack of accuracy and fidelity, because the discharge changes the surface state of the electrodes, leading to a change of the electron emission of the cathodes (secondary emission and field emission). Besides, it gives nonlinear indications in terms of pressure, the discharge being both the cause and the effect of the ionization. It is chiefly an industrial gauge.

6.5.3. **The hot-cathode triode gauge**

6.5.3.1. *Principle*

This is a classical tungsten filament radiotriode. It allows one to separate the functions of ionization (due to electrons emitted by the filament) and of ion collection, both being mingled in the Penning gauge.

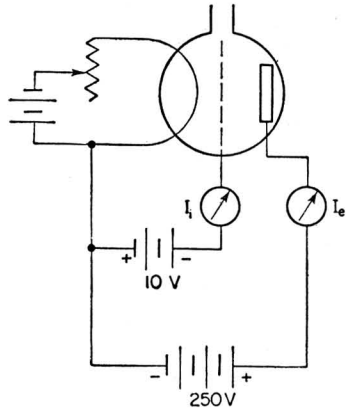


FIG. 6.24

A first possible electrical circuit is that of Fig. 6.24. The electrons emitted from the filament are collected by the plate, whilst the ions produced are gathered by the grid, the ion current being measured by a microammeter. This current indeed gives a measurement of pressure.

Most of the time, one prefers to reverse the parts of the grid and the plate, the first one collecting electrons and the second one collecting ions (Fig. 6.25). The sensitivity is so increased by a coefficient 4 or 5, perhaps because the

efficiency of the ion collection by the plate is better, perhaps also because electrons make a series of oscillations from both sides of the grid before they are gathered by it, which increases their path length.

Whatever may be the circuit used, the electron collector is at a potential of about +250 V, the ion collector at about −20 V.

The electron current is adjusted by controlling the filament current.

A simple calculation will give the order of magnitude of the collected ion current. Take an electron current of 10 mA, a distance from filament to electron collector of 1 cm, a pressure of 10^{-5} mm Hg, an ionization probability of 10%.

The total number of electrons travelling, per second, from the cathode to the collector is:

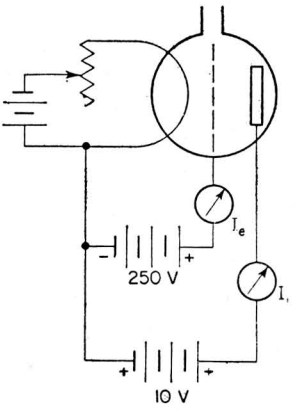


FIG. 6.25

$$N_e = \frac{10\times10^{-3}}{1{\cdot}6\times10^{-19}} = 6{\cdot}25\times10^{16} \text{ electrons per sec.}$$

The total path they cover per second is then $6{\cdot}25\times10^{16}$ cm.

At 10^{-5} mm Hg, the mean free path of electrons in air is 4000 cm.

The number of collisions of electrons on molecules will be consequently:

$$N_c = \frac{6{\cdot}25\times10^{16}}{4000} = 1{\cdot}56\times10^{13} \text{ collisions per sec}$$

and the number of ions produced:

$$N_i = 1{\cdot}56\times10^{13} \times \frac{10}{100} = 1{\cdot}56\times10^{12} \text{ ions per sec.}$$

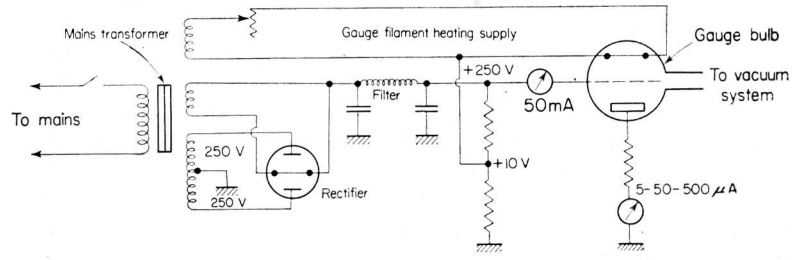


FIG. 6.26

Then, the ion current will be:

$$I_i = 1{\cdot}56 \times 10^{12} \times 1{\cdot}6 \times 10^{-19} = 2{\cdot}5 \times 10^{-7}\ \text{A or } 0{\cdot}25\ \mu\text{A}.$$

It follows that with a sensitive galvanometer and with an electron current of 20 to 50 mA, a pressure of 10^{-7} mm Hg will be easily measured.

A complete supply from the mains is easily realized (Fig. 6.26).†

The calibration is nearly linear in terms of pressure, as the type curves of Fig. 6.27 show.‡

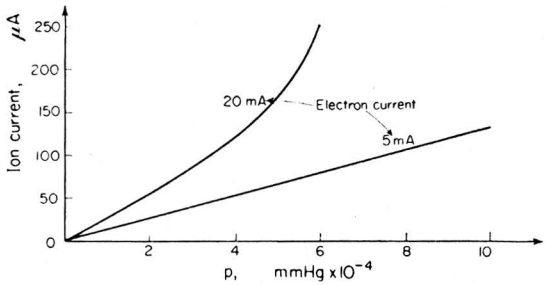


FIG. 6.27

However, if one works with relatively high pressures ($> 10^{-4}$ mm) and with large electron currents (> 10 mA), the ion current is observed to rise more quickly than pressure, because a "chain ionization" takes place.

6.5.3.2. *Advantages and Disadvantages*

The main advantage of the triode gauge is its good accuracy due to the linearity of its reading in terms of pressure in the range covering 10^{-6} to 10^{-3} mm Hg.

The disadvantages are mostly due to the possible breaking of the incandescent filament in the case of sudden air input. Besides, the accuracy may be altered by the following causes:

(a) Every time there is an electric discharge in a gas, there is a pressure fall due to absorption by the electrodes (see Sec. 4.3.4). If the gauge is not connected to the vacuum system by a large diameter tube, the

† This diagram is taken from Ch. Biguenet's book: *Les Cathodes chaudes*. Editor: *Revue d'Optique*, Paris, 1947.

‡ After J. Yarwood (5).

pressure in the gauge may be noticeably lower than in the other parts of the vacuum circuit. This phenomenon is evidently more striking when the electron current is highest.

(b) On the other hand, under the effect of electron bombardment, the electron collector may be heated and may release occluded gases disturbing the measurement. It is then required, before each measurement, to out-gas the gauge carefully either by heating, or by a heavy electron bombardment (on all gauges a commutator allows one to operate this bombardment).

(c) At very low pressures ($< 10^{-7}$ mm Hg) electrical leakages of the ion collector may alter measurements.

(d) Also for these low pressures, important errors may be due to photo-electric emission of the ion collector under the effect of the soft X-rays, emitted by the electron collector when struck by electrons accelerated under a few hundred of volts.

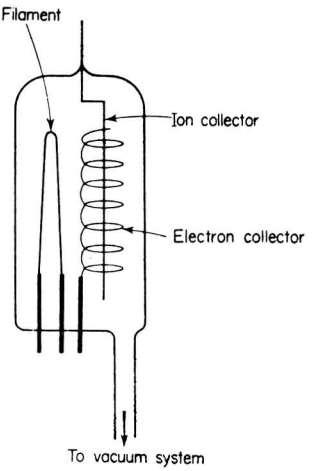


FIG. 6.28

6.5.3.3. *A Variant*: *The Bayard and Alpert Gauge*

To allow accurate measurements at low pressures, Bayard and Alpert designed a gauge (Fig. 6.28)† in which the ion collector is reduced to a fine tungsten wire, set on the axis of a metallic grid used as an electron collector. The emitting filament is put outside the grid. Further, the anode voltage is lowered to 100 V.

Thanks to these various precautions, X-ray emission is greatly reduced; their interception by the ion collector is decreased in a ratio of 100 in comparison with a normal gauge and all the generated ions are collected by the axial wire.

The authors point out their gauge allowed them to make accurate measurements to about 10^{-10} mm Hg.

6.5.4. **The radioactivity gauge or alphatron gauge**

The ionizing agent here is constituted with particles emitted by a radioactive source (generally a Cobalt 60 source). The ions pro-

† Bayard and Alpert. *Rev. Sci. Instr.* **21**, 572, 1950.

duced are collected by a collector raised to a voltage of about −200 V with respect to the source (Fig. 6.29).

However, the ion current obtained being very low (of about 10^{-10} A

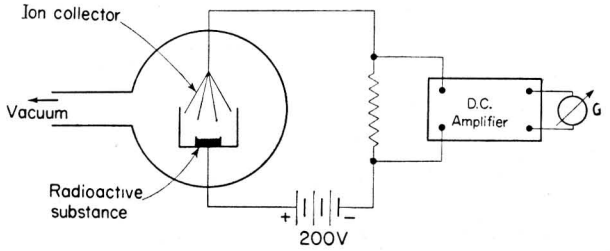


FIG. 6.29

for a pressure of 1 mm Hg), it is necessary to amplify it with the help of a d.c. amplifier.

The deflexion of the output galvanometer is nearly proportional to the pressure, but notably depends on the nature of gases (Fig. 6.30).

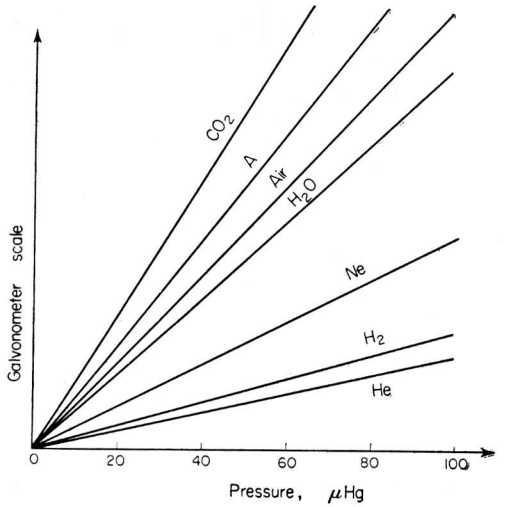


FIG. 6.30

The measurement range is approximately the Pirani gauge one: 10^{-3} to 10 mm Hg.

This apparatus is very robust, as it has neither a moving part nor a heating filament.

CHAPTER VII

VACUUM TECHNIQUE SYSTEMS

After having studied the processes used to obtain low pressures (pumps) and to measure them (manometers), it remains to describe how to bring together these various elements to realize a pumping system.

Besides, these elements are all connected together by pipes which play an important part for the proper working of the system.

On the other hand, a pumping system generally includes several pumps as well as a number of indispensable appliances.

Consequently, this chapter will have the following subdivisions:

1. The calculation of vacuum pipes;
2. The grouping of pumps;
3. The components used in vacuum technique (stop-cocks and valves, joints and gaskets, traps, etc.);
4. The description of a complete pumping-system;†
5. Ultra-high vacuum problems.

7.1. CALCULATION OF LOW PRESSURE PIPES

7.1.1. Definition of the conductance of a pipe

Consider a pumping system of a vessel connected to a pump by a pipe (Fig. 7.1).

The speed S of a pump has been defined (see Sec. 5.1.1.2.) as the volume of gas it may exhaust per second at a given pressure, this volume itself being measured at this same pressure. It is evident that the placing, between the pump and the

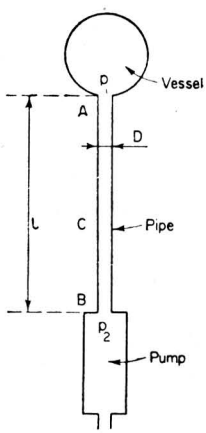


Fig. 7.1

† The particular case of the use of such a system for electron tube pumping will not be studied. This will done in Vol. II, Sec. 14.3.

vessel, of a tube with a more or less large diameter will slow down the gaseous flow and consequently will reduce the true pumping speed.

To calculate this true speed, a new quantity U, called the *conductance* of the tube† will be introduced; it will be defined as being *the volume of gas which flows through the tube subjected to a pressure difference* $p_1 - p_2$, *this volume itself being measured at the pressure* $p_1 - p_2$.

7.1.2. The true speed of a pumping system

With this definition, the true speed S' of a pumping system is given by the following formula, which is valid for all pressures:

$$\boxed{\frac{1}{S'} = \frac{1}{S} + \frac{1}{U}} \,. \tag{7.1}$$

In fact, let μ be the mass of gas exhausted by the pump per second. It is of course the same at all parts of the circuit, as well as in C or in B (Fig. 7.1).

Regarding the mass of gas flowing through the pipe, at C for instance, one obtains:

$$\mu = U\,(p_1 - p_2)\,\frac{M}{RT}\,. \tag{7.2}$$

The same mass at the outlet of the vessel gives:

$$\mu = S'\,p_1\,\frac{M}{RT}\,. \tag{7.3}$$

Also, the same mass at the inlet of the pump gives:

$$\mu = S\,p_2\,\frac{M}{RT}\,. \tag{7.4}$$

Combining these three equations, it follows that:

$$\frac{1}{S'} = \frac{1}{S} + \frac{1}{U}\,. \tag{7.1}$$

7.1.3. The grouping of pipes

The conductance resulting from an assembly of pipes connected in series is easily checked to be:

$$\frac{1}{U} = \frac{1}{U_1} + \frac{1}{U_2} + \frac{1}{U_3} + \cdots. \tag{7.5}$$

† The conductance is also called the *unit flow*, because it is also the flow of a tube submitted to a difference of the pressure equal to unity, the volume of flow being measured at the unit pressure.

If the elements are parallel-connected, the result is:

$$U = U_1 + U_2 + U_3 + \cdots . \tag{7.6}$$

One may point the formal analogy with electric conductance.

7.1.4. Calculation of the conductance of a pipe

7.1.4.1. *Viscous Flow*

It has been seen (Sec. 2.4.1.1) that in viscous flow, the mass of gas passed by a tube per sec is:

$$\mu = \frac{\pi r_0^4}{8 \eta l} (p_1 - p_2) \left(\frac{p_1 + p_2}{2} \right) \frac{M}{R T} . \tag{2.108}$$

From eqs. (7.2) and (2.108), it is deduced:

$$U = \frac{\pi r_0^4}{8 \eta l} \frac{p_1 + p_2}{2} . \tag{7.7}$$

In the case of air, $\eta = 1{\cdot}6 \times 10^{-4}$ C.G.S.; whence, introducing the diameter D:

$$\boxed{U = 152 \frac{D^4}{l} \left(\frac{p_1 + p_2}{2} \right)} \tag{7.8}$$

taking U in cm³/sec, D and l in cm, p_1 and p_2 in baryes.

7.1.4.2. *Molecular Flow*

In this case (Sec. 2.4.1.2) the mass of gas flowing through a tube has been seen to be, per sec:

$$\mu = \frac{8 r_0^3}{3 l} (p_1 - p_2) \sqrt{\left(\frac{\pi M}{2 R T} \right)} . \tag{2.119}$$

As above, it is deduced:

$$U = \frac{8 r_0^3}{3 l} \sqrt{\left(\frac{\pi R T}{2 M} \right)} . \tag{7.9}$$

In the case of air at 20°C, $M = 29$, $T = 293$°K; whence, introducing the diameter D:

$$\boxed{U = 11{,}600 \frac{D^3}{l}} \tag{7.10}$$

taking U in cm³/sec, D and l in cm.

7.1.4.3. *Intermediate Flow*

Knudsen showed that when the mean free path is of the same order of magnitude as the diameter of the pipe, the conductance is given by the complex formula:

$$U = \underbrace{\frac{\pi}{128\,\eta}\frac{D^4}{l}\,p}_{1} + \underbrace{\frac{1+(D\,p/\eta)\sqrt{(M/R\,T)}}{1+1{\cdot}24(D\,p/\eta)\sqrt{(M/R\,T)}}}_{2}\ \underbrace{\frac{1}{3}\sqrt{\left(\frac{\pi\,R\,T}{2\,M}\right)}\frac{D^3}{l}}_{3} \qquad (7.11)$$

in which p is the mean pressure $(p_1 + p_2)/2$, the other letters representing the same quantities as above.

At low pressures, it is obvious that term 1 becomes negligible, term 2 tends to unity and the formula reduces to term 3 of molecular flow.

At the opposite, for high pressures, term 2 is still tending to unity, so that term 1 (viscous flow) becomes the prevailing one.

7.1.4.4. *The Choice of the Formula to be Used*

A criterion due to L. Dunoyer† allows the choice of the formula to be used, for the calculation of conductance, in terms of pressure and the diameter of the pipe.

Taking p in baryes and D in cm:

If $p \times D > 617$, the formula of viscous flow is to be applied.

If $p \times D < 23$, the formula of molecular flow is to be applied.

Lastly, if:

$$23 < p \times D < 617$$

(which is the case of intermediate flow), the following simplified formula may be applied:

$$U = 140\,\frac{D^4}{l}\,p + 10^4\,\frac{D^3}{l}\,. \qquad (7.12)$$

In the three cases, the maximum error is 10%.

The curves of Fig. 7.2 allow us to calculate the conductance of pipes of length 1 m, with diameters lying between 0·1 and 10 cm.

7.1.4.5. *Some Remarks on the Variation of the Conductance in Terms of Pressure*

Note that the viscosity of a gas enters in the formula of viscous flow, and not the molecular mass nor the temperature of the gas; it is the opposite which occurs in the formula of molecular flow.

† L. Dunoyer. *Le Vide*, No. **30**, 881, 1950.

In addition, *the conductance depends linearly on pressure for viscous flow, but not for molecular flow.*

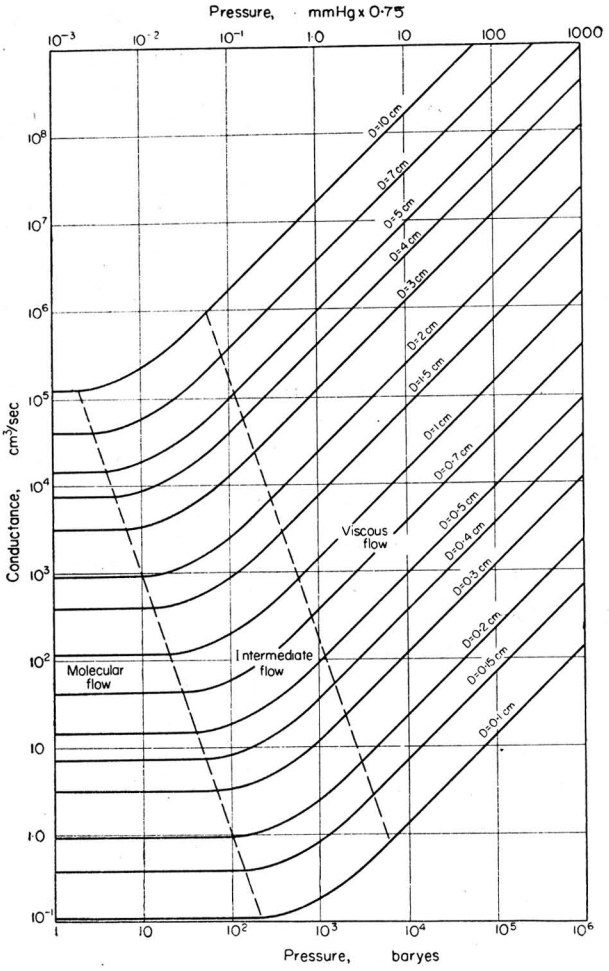


FIG. 7.2. Conductance of 1 m length pipes.

A remarkable phenomenon arises out of the formula stated by Knudsen for intermediate flow: the value of the conductance passes through a minimum (very slight indeed), when the pressure decreases,

and then slightly increases to a value independent of pressure when this latter is low (Fig. 7.3).

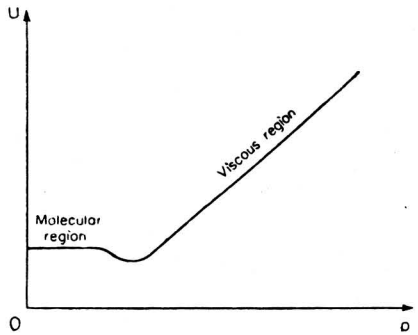


FIG. 7.3

By deduction from Knudsen's formula, in the case of air, this minimum is found to occur when the pressure is such that the mean free path is equal to about 2·5 times the pipe diameter.

7.1.5. Practical Applications

7.1.5.1. *Viscous Flow*

Let a vane-type rotary oil pump with a speed of 3·6 m³/hr around 1 mm Hg be connected to a diffusion pump, which it must back through a pipe length of 1 m.

What will be the true speed (at the end of the pipe on the side of the diffusion pump), according as the diameter is 5 mm or 20 mm? The mean pressure in the pipe is supposed to be 1 mm Hg.

Solution: for $D = 0{\cdot}5$ cm:

$$U_1 = \frac{152 \times 0{\cdot}5^4 \times 1333}{100} = 127 \text{ cm}^3/\text{sec};$$

For $D = 2$ cm:

$$U_2 = \frac{152 \times 2^4 \times 1333}{100} = 32{,}400 \text{ cm}^3/\text{sec}.$$

In the first case, the pumping speed is brought back from 1 l./sec to:

$$S'_1 = \frac{S\,U_1}{S + U_1} = 0{\cdot}113 \text{ l./sec}$$

i.e. reduced to 1/9 of the pump speed. In the second case, on the contrary, the pumping speed becomes:

$$S'_2 = 0{\cdot}97 \text{ l./sec}$$

and is thus in practice unchanged.

7.1.5.2. *Molecular Flow*

(a) Consider a diffusion pump with an exhaust speed of 3 l./sec. It is used to exhaust a bulb, to which it is connected by a pipe of 1 cm

diameter. What can be the maximum length so that the pumping speed is reduced only by half?

ANSWER: The conductance of the stem must be equal to 3000 cm^3/sec at least. It is found that the length must be less than 3·9 cm.

(b) "Miniature" electron tubes are exhausted by means of pipes with a length of 6 cm and an inner diameter of 2 mm. Application of Dunoyer's formulae shows the flow is molecular for all the pressures below 0·1 mm Hg, which is nearly always the case. In these conditions, the conductance of these pipes is 15 cm^3/sec. Then the pumping speed is practically independent of the performance of the diffusion pump.†

7.2. THE GROUPING OF PUMPS

7.2.1. **Principles**

The connecting of a diffusion pump to a fore-pump which must back it will now be discussed.

The single condition to be observed is that, in all the normal working conditions of the diffusion pump, the fore-pump should be to keep a pressure lower than the backing pressure p_0 of the diffusion pump.

From that, the two following consequences result:

(a) the limiting pressure of the fore-pump must be lower than p_0.

(b) the mass flow of the fore-pump, at a pressure a little below p_0, must be higher than the maximum flow in mass of the diffusion pump.

7.2.2. **The method for the choice of a fore-pump**

For the diffusion pump, the starting point is the curve $S = f(p)$ of the pumping speed in terms of pressure. It is experimentally determined, or the one given by the maker is used, if it is considered reliable.

Let us take the example of Fig. 7.4 . Firstly, it is deduced that the diffusion pump will not be backed if the fore-pressure rises higher than 10^{-1} mm Hg.

† The reader's attention is drawn to the fact that this is true only at molecular flow. At the beginning of the pumping process, the flow may become viscous, owing to the great quantities of gas to remove: then, the speed of the pump may play again an important part.

On the other hand, the curve is seen to present a flat horizontal part between 10^{-3} and 10^{-5} mm Hg. The mass flow being connected to the flow in volume (or pumping speed) by:

$$D_m = S\,p\,\frac{M}{R\,T} \tag{7.13}$$

it is seen that to take the maximum profit from the performance of the diffusion pump, the fore-pump must have a mass flow higher or equal to the maximum of the mass flow of the diffusion pump, when

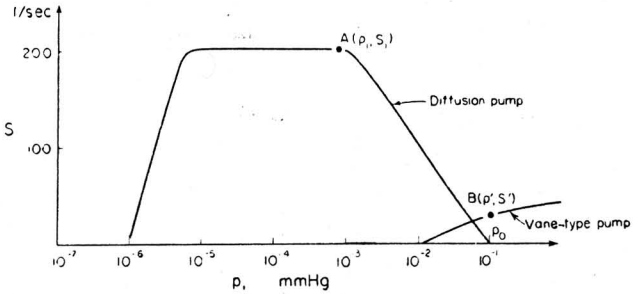


FIG. 7.4

the speed of the latter is at its maximum. In other words, the mass flow at point A must be calculated, and that of the fore-pump must be at least equal to it.

In fact, as the exhausted gas and temperature are nearly the same for both pumps, it will be written, by applying Boyle's law:

$$S'\,p' \geq S_1\,p_1 \tag{7.14}$$

(S' and p' corresponding to the fore-pump; S_1 and p_1 to the diffusion pump).

For example, let us use the fore-pump (a vane-type pump) of which the end of the curve $S' = f(p')$ is seen at the right of Fig. 7.4.

First, we see that its limiting vacuum is 10^{-2} mm Hg, which fulfils the first condition.

Secondly, at 5×10^{-2} mm Hg, the speed is seen to be 25 l./sec. Then the above inequality is rightly fulfilled, as:

$$5 \times 10^{-2} \times 25 > 200 \times 10^{-3}.$$

Note that it is advisable to use, as in the above example, a fore-pump 5 to 10 times more efficient than is strictly necessary, in order

to avoid any loss of backing of the diffusion pump in the case of a too sudden gas flow.

7.2.3. The use of intermediate pumps (booster pumps)

When high speed diffusion pumps have to be used, the condition to realize a low fore-pressure with a high flow, would lead to the use of vane-type pumps with prohibitive dimensions.

In this case, between the vane-type pump, and the diffusion pump, is set an ejector pump described in Chapter V which requires only a fore-pressure of about 10 mm Hg. That allows one to make the vane-type pump work in a range of pressures in which its mass flow is high. The pump dimensions are thus very much reduced.

7.2.4. The influence of pipes upon the grouping of pumps

When the fore-pump which has to back the diffusion pump is calculated, it is necessary to ensure that the tube connecting the two pumps does not reduce prohibitively the speed of the fore-pump. To check it, the formulae given at the beginning of this chapter can be used, taking into account the fact that, in the case considered, the flow is always of the viscous kind.

7.3. APPLIANCES USED IN VACUUM TECHNIQUE

7.3.1. Joints

Joints are used to connect tightly together two pipes or a pipe to an apparatus such as a pump, a bell-jar, etc.

According as to whether the joints are definitely sealed, or easily dismantled, they are classified into fixed joints and demountable joints.

7.3.1.1. *Fixed Joints*

They are mostly obtained by sealing; it is of course the best way to have perfect tightness.

In this way glass tubes are connected end-to-end by blow-pipe heating and also pipes to a glass vessel (Fig. 7.5). The elementary

precaution of not sealing together glasses with expansion coefficients differing by more than 5%, must be observed (see Vol. II, Sec. 12.2.1).

In the case of metallic tubes, one may use either oxyacetylene welding (for steel tubes), or silver-brazing or tin-soldering in the case of copper tubes.

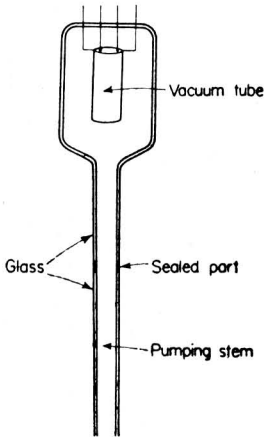


FIG. 7.5

In the same way a glass tube may be connected to a metallic tube by a non-demountable sealing, but this peculiar problem of metal-to-glass sealings will be treated in Vol. II, Sec. 14.2.5).

7.3.1.2. *Demountable Joints*

These are joints and gaskets allowing one to connect or separate low-pressure devices without calling on specialists (glass-blowers, arc-welders, etc.).

Picein joints. Two tubes may easily be joined together with the help of a picein joint: for this, tubes with different diameters are used so that they fit into each other. Then the junction is covered with picein by a light heating with a soft flame† (Fig. 7.6a) (picein is sold in sticks and it melts at 50°C) (see Sec. 7.3.5).

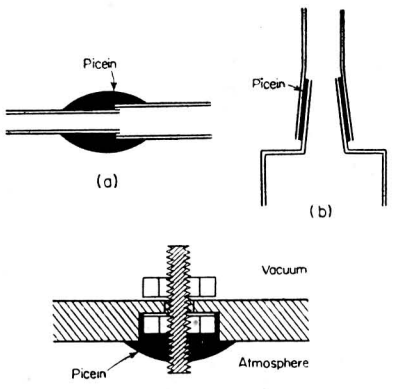


FIG. 7.6

In laboratories, diffusion pumps are very often connected to their piping by using the same procedure. The pump is provided with a ground male cone and the vacuum pipe with a ground female cone. Some melted picein is placed between the cones‡ (Fig. 7.6b).

Again, in the same fashion, the

† A flame of a gas burner without any air admission.

‡ During operation of the vacuum system, the heating of a picein joint must be carefully avoided because: (*a*) the vapour pressure of this product, negligible at 20°C, rises very quickly with temperature; (*b*) if picein becomes soft, the atmospheric pressure will make it run inside and the joint will be broken off.

conducting leads traversing the insulating wall of a vacuum vessel may be made air-tight (Fig. 7.6c).

Lastly, in the case of a leaks in a system, it is to be mentioned that picein joints can always be considered as doubtful, because this substance becomes cracked in the long run. From time to time, these joints have to be remade.

Rubber gaskets. They are used in industrial systems for quick mounting and demounting. For large diameter pipes, flat gaskets are used; they are pressed down by bolts and screws (Fig. 7.7).

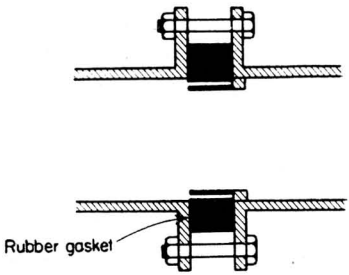


FIG. 7.7

For small pipes, threaded unions or ring-junctions are used with toroid gaskets (Fig. 7.8).

Also, flat or toroid gaskets of a large diameter are used to seal evaporation bell-jars, at the place where they are applied on their mounting plate (a ledge has to be provided on the latter to avoid the gasket from sliding to the inside of the bell-jar under the effect of atmospheric pressure) (Fig. 7.9).

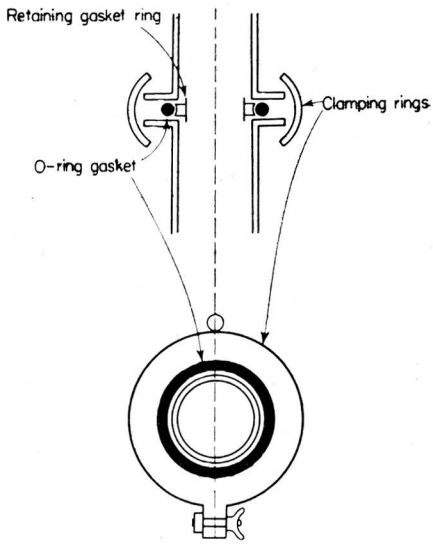


FIG. 7.8

Two interesting applications of rubber gaskets in industrial diffusion pumps have to be mentioned.

The device of Fig. 7.10a allows one to connect instantaneously the pumping stem of an electron tube to the diffusion pump; the stem passes through a rubber ring held on its perimeter. If this ring is compressed with the help of a screw, since the rubber can expand only towards its axis, it closely encloses the stem and ensures the tightness (a ball bearing

transmits the longitudinal effort to the ring without exerting any torsion).

Figure 7.10b represents a similar device used for the joining of certain industrial diffusion pumps.

Ground and greased unions. They are made of male and female cones. They can be dismantled still more quickly than picein joints, but they require a perfect grinding of the surfaces in contact, as well

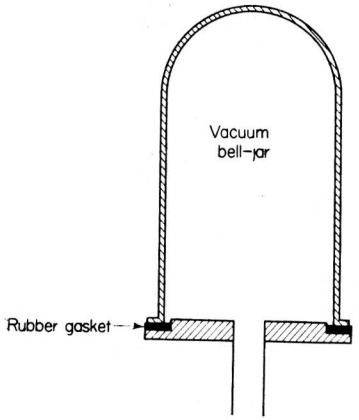


FIG. 7.9

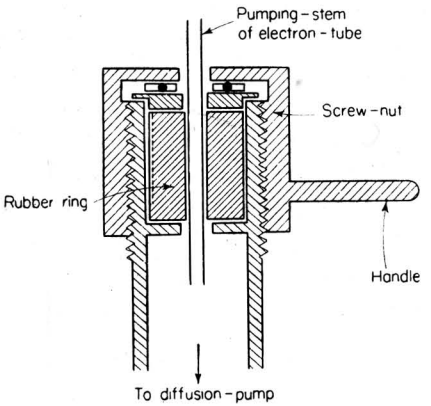


FIG. 7.10a

as the use of a very good vacuum grease (Fig. 7.11). They are made of glass or metal.

Metal gaskets. For very low pressures, metal gaskets are more and more preferred to rubber or greased gaskets, because they have extremely low vapour pressures. They are of two kinds: the soft metal gaskets, and the knife-edge seals.

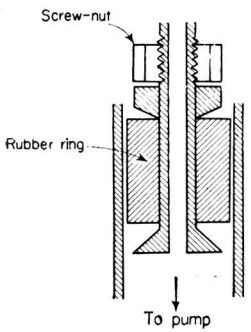


FIG. 7.10b

1. *Soft metal gaskets*

They consist of a soft metal ring squeezed between the two flat parts to be joined together. The metal used may be indium, lead or aluminium. Indium is particularly convenient for this use because of its softness and very low vapour pressure. For example, a bell-jar may be made air-tight with a circular gasket obtained by twisting together several indium wires. The string so obtained is

squeezed between the bell-jar edge and the mounting plate by means of bolts and screws.

After the gasket has been used and demounted, indium is easily retrieved and drawn again into wire.

2. *Demountable knife-edge seals*

These are demountable seals using molecular inter-diffusion phenomena which occur between soft metals submitted to high pressures combined with high temperatures (but below the melting point).

Let us assume that a copper container has to be closed tightly with a top of the same metal, provided that the latter could be removed if needed. The top is machined so that a circular sharp edge is made on its circumference (Fig. 7.12). This edge and the corresponding plate part of the container are both gold-plated. The top is then pressed on the container by means of bolts and screws, so that the edge penetrates into the opposite metal. By heating to 600°C, diffusion from both the cover and the container takes place, and air-tightness is achieved. However, the top may be removed if necessary. In this case, the knife-edge must be machined and gold-plated again before being re-used.

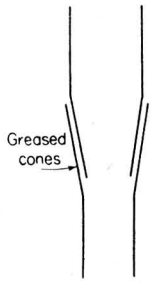


FIG. 7.11

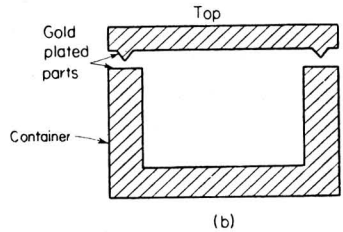


Fig. 7.12

7.3.2. **Taps and valves**

These appliances are used to separate from each other certain parts of a pumping system.

They are built in two or three-way types (or even more), depending on whether they have only to cut off a gaseous current, or to behave as a selector-switch, i.e. to join a pipe to several chosen vessels (Fig. 7.13).

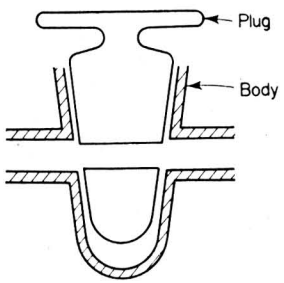


FIG. 7.13

Small taps and cocks are generally made of glass for laboratory purposes. The body and movable parts, in a conic shape, are

emery-ground one against the other, and then coated with vacuum grease.

For large sized industrial systems, the valves used are designed to have a conductance as good as possible. They are usually made of stainless steel. Figure 7.14a shows a pattern. The tightness of the closing screw is achieved by tombac†, an elastic bellows made of 72% Cu + 28% Zn alloy.

For ultra-high vacuum applications, it is necessary to bake-out all the components of the vacuum system

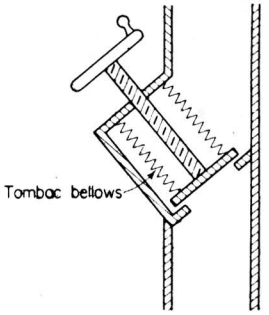


FIG. 7.14a

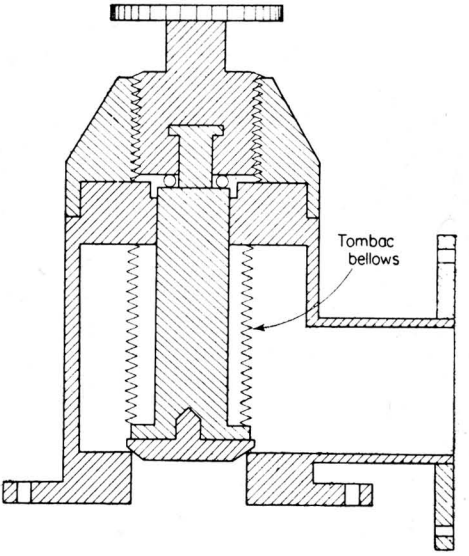


FIG. 7.14b

(see Sec. 7.5.1). Figure 7.14b shows a bakeable vacuum valve developed at Westinghouse Research Laboratories. It may be baked-out to 450°C. In order to avoid "seizing", the fixed parts (the screw-nut and the seat) are of copper, while the moving ones (the screw and the nose) are made of stainless steel.

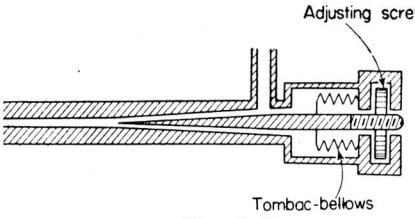


FIG. 7.15

Sometimes it is required to admit into the vacuum system small quantities of gas. For that purpose a gas admittance valve is used; it is constructed as indicated in Fig. 7.15. The closing is obtained with a needle, so that a long movement is required to produce a small admittance.

† Originally, the word "tombac" was used to mean only the particular alloy of tin and copper. Now it is applied to the bellows made with this metal.

7.3.3. Traps

Traps, as seen before, are used to condense the vapours of mercury, water, oil, and also to avoid their introduction into the vessel to be exhausted. Most of the time, they consist of a glass tube with double walls arranged as baffles. The external tube is immersed in liquid nitrogen† (−180°C) contained in a Dewar flask.‡ Gases then have to travel along strongly cooled walls (Fig. 7.16a).

In another system, the trap itself is used as a vessel for liquid nitrogen (Fig. 7.16b).

If there is any difficulty with the supply of liquid nitrogen, it is to be mentioned that the use of dry ice (solidified carbon dioxide gas) gives almost as good results.

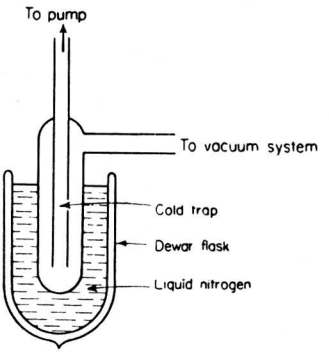


FIG. 7.16a

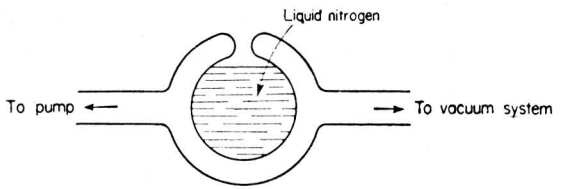


FIG. 7.16b

The temperature obtained is −78°C. Dry ice may be easily made by covering the orifice of a cylinder of compressed CO_2 with a bag of tight texture, and by opening the tap (Fig. 7.17): the expansion of the gas produces a cooling sufficient enough to solidify a part of it. To ensure a good thermal contact between the trap and the refrigerant, it is required to mix the dry ice with acetone.

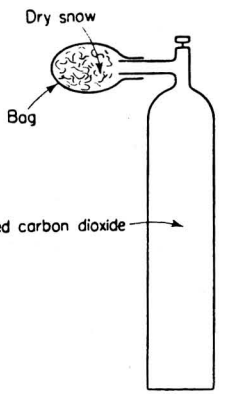


FIG. 7.17

† Liquid nitrogen, as opposed to liquid air, gives no risk of explosion.

‡ A Dewar flask is a double wall glass vessel. Vacuum is provided between the two walls and they are silver-plated: thus heat losses by conductivity as well as by convection and by radiation are reduced. It is the principle of Thermos flasks.

The liquid air trap must be provided with dimensions large enough to prevent slowing down of the speed of the pumps to which they are connected because of their very low conductance.

7.3.4. The transmission of a movement through a vacuum vessel

Very often it is necessary to transmit a mechanical force (translation or rotation) through the walls of an exhausted vessel. Several solutions are possible:

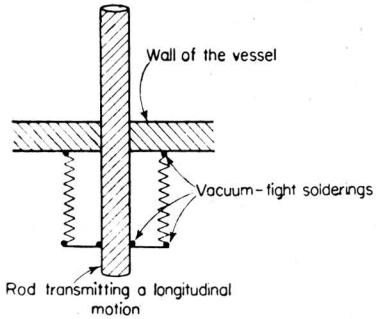


FIG. 7.18

7.3.4.1. *The Tombac*

It has been seen above (see Sec. 7.3.2) that this is the name of a bellows made of a copper–zinc alloy. It allows one to achieve some translation movements with excellent conditions of air-tightness (Fig. 7.18).

The reliability of this device is so good that it is possible to make sealed-off electron tubes provided with a tombac allowing one to vary, from the outside, certain performances of the tube by shifting particular electrodes.

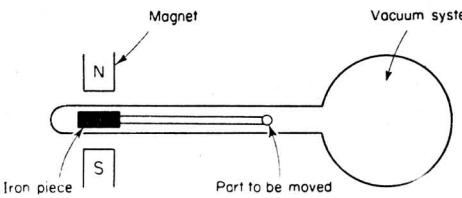


FIG. 7.19

7.3.4.2. *Magnetic Processes*

It readily comes to mind to act through a glass bulb on an iron piece, by using an external magnet.

In this way, a "probe" may be moved during the manufacture of television camera tubes (see Vol. II, Sec. 15.3).

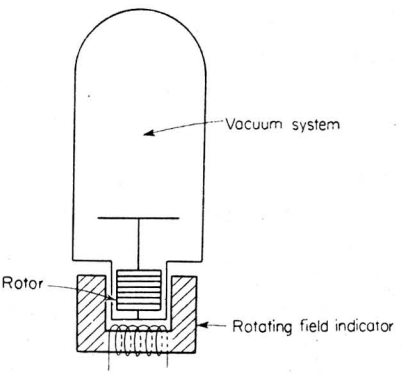


FIG. 7.20

A continuous movement of rotation may be obtained with a rotating field, created outside by an adequate system of coils, which can, inside the glass vessel (or through a thin non-magnetic metal wall), put a rotor into rotation (Fig. 7.20).

7.3.4.3. *Ground Joints*

A device with a conical grinding similar to the one used for taps, allows one to transfer, from the outside to the inside of a vacuum chamber, a movement of rotation or of translation (Fig. 7.21).

7.3.4.4. *The Wilson Seal*

This is a rubber disk drilled in its centre with a hole slightly smaller than the axis going to traverse it: the result is that the axis being in place, the joint takes nearly the shape of a truncated

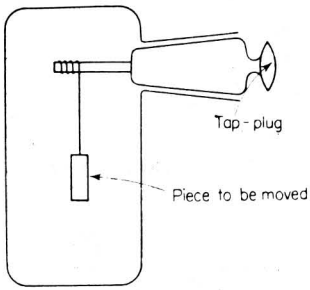


FIG. 7.21

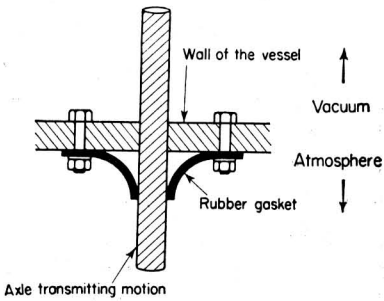


FIG. 7.22

cone, the small base of which is turned in the direction of the outside. Atmospheric pressure then strongly presses the gasket on the axis, allowing the latter to rotate with sufficient tightness (Fig. 7.22).

Note that both these systems, because of the risks of leak offered by the grinding or by the gasket, are applied only to experimental mountings permanently connected to a pump.

7.3.5. Sealing products used in vacuum technique†

Picein is a mixture of beeswax and of purified coal-pitch. It is solid at 20°C and it melts at 50°C. At 20°C, its vapour pressure is about 10^{-8} mm Hg and at 50°C is over 1 mm Hg.

De Khotinsky cement is another plastic product which is made of about 15 parts of pine tar and 85 parts of shellac. It melts at a higher temperature and is much harder than picein.

Araldite is a synthetic resin available in sticks, powder or varnish. It has a good adhesion to glass, mica, ceramics and metals (for instance it may be used to seal a vacuum-tight window to a metal bulb). It

† J. Yarwood (5), p. 176 and 191.

may be employed also in all the uses of picein with more reliability, but the demounting of the sealed pieces is more difficult than with picein.

Solid Araldite melts at about 120°C. Whatever may be the kind used, it must be polymerized, for example, by heating it for 10 min at 240°C, then for 20 min at 220°C, for 1 hr at 190°C and finally for 2 hr at 180°C.

Grease Apiezon L (marketed by Shell Chemicals Ltd) is used to make glass stop-cocks air-tight or rubber-to-glass junctions. It has a vapour pressure of 5×10^{-6} mm Hg at 20°C.

Silicone greases marketed by Dow Corning Inc. are remarkably stable in terms of temperature. Their viscosity remains constant between -40 and $+200$°C. They do not harden in the long run and their very low vapour pressure allows one to use them to obtain vacua of about 10^{-6} mm Hg.

Rubber is commonly used to make fore-vacuum pipes. It always releases a little hydrogen. It is advisable to boil it before use in a solution of caustic soda, then to wash and to dry it. Even in these conditions, its vapour pressure is about 10^{-4} mm Hg. However, using it as a gasket for a bell-jar with a high-speed diffusion pump, it enables one to get pressures down to 10^{-5} mm Hg.

7.4. DESCRIPTION OF A PUMPING SYSTEM

It is evident that the components of a pumping system will vary according to the objective to be carried out.

As an example, a small laboratory equipment will be described allowing us to realize all kinds of operations bringing vacuum technique into play, such as:

Exhausting of small vessels, such as experimental electron tubes (this operation will be studied in detail in Vol. II, Sec. 14.3).
Coating of glass objects with thin metal layers in order to make them good electrical conductors.
Manufacturing of mirrors.
Anti-reflecting treatment of optical lenses.
Out-gassing of small metal pieces, etc.

7.4.1. General arrangement

Figure 7.23 shows the assembly of the system. A mounting frame of about 1 m height, width 1·5 m and depth of 0·8 m, is used to support the various apparatus.

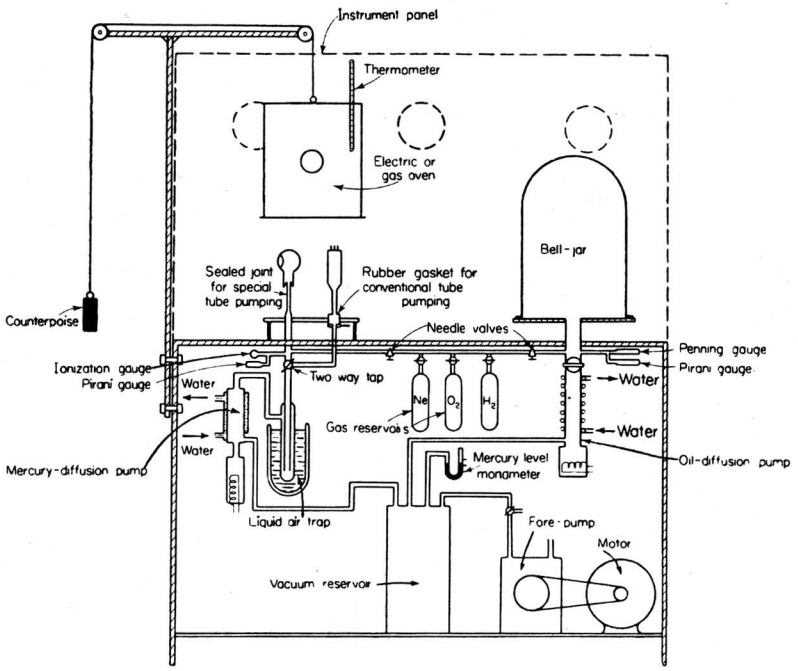


FIG. 7.23. Standard pumping system for laboratory use.

This frame is a metal table, the horizontal part of which is lined with an asbestos plate 20 mm thick.

The pumps and their appliances are put under the table, and the vessels to be exhausted overhead.

A vertical board set backwards supports the different supplies providing the currents and voltages required for the various operations.

7.4.2. The pumps used

A vane-type pump with a speed of about 2000 to 4000 l./hr produces in a metal reservoir with a volume of some litres, a fore-vacuum of

about 0·1 mm Hg able to back the diffusion pumps. Thus a vacuum storage is obtained which can avoid the vane-type pump working permanently.

An oil diffusion pump with a speed of 10 l./sec at 10^{-4} mm Hg is used to exhaust a vacuum bell-jar. In the latter, one can do evaporation in vacuum, cathode sputtering, etc. (on the right-hand side of the table).

On the left side, a mercury diffusion pump having a speed of the same order at 10^{-2} mm Hg will enable the exhausting of small vessels such as electron tubes.

Both these pumps are provided with a liquid-air trap.

7.4.3. **Working arrangements**

The oil diffusion pump is connected to the base of a glass evaporation bell-jar with a diameter of about 30 cm. Air-tightness is very efficiently obtained by grinding the flange of the bell-jar upon the base. The surfaces in contact are carefully greased with silicone grease.

As for the mercury diffusion pump, it will serve for the exhausting of electron tubes. For this purpose it is fitted with two kinds of connections:

One using a rubber joint, of the kind indicated in Fig. 7.10, will serve to pump conventional tubes using getters.

A second for a glass-to-glass seal will serve to exhaust the tubes requiring a very high vacuum, and in which a getter cannot be used (photocells, etc.).

The pressure measurement at the different parts of the system is obtained in the following ways:

(a) A U-shaped manometer is connected to the vacuum reservoir. It is provided with an electric switch connected to a bell which rings when the pressure rises higher than 2 to 3 mm.

(b) To the evaporation bell-jar are connected on the one hand a Pirani or a thermocouple gauge used, for example, for cathode sputtering; on the other hand, a Penning gauge which is used for evaporation in vacuum.

(c) Lastly, on the side of the mercury diffusion pump there is also a Pirani gauge for the filling of gas tubes, and an ionization gauge for high vacuum measurement.

7.4.4. Subsidiary components

Besides the essential appliances described above, a certain number of very useful components will be added:

(a) On a vertical board set at the back of the frame:

a supply furnishing the following voltages: 10, 20, 50, 100 volts (a.c.) with a power of about 100 watts. It will enable the heating of the filaments of the tubes to be exhausted, or of the filaments used to evaporate products in vacuum;

a 300 V, 100 mA d.c. supply for cathode formation during pumping;

a 2000 V, 10 mA d.c. supply for cathode sputtering, formation of gas discharge tubes, etc.

These three supplies will include voltage control systems.

(b) A high-frequency generator, described in Chap. VIII, with an operating power of about 2 kW, for the out-gassing of metals in vacuum, the flashing of getters, etc.

(c) An electric or gas oven, of about $40 \times 40 \times 40$ cm, permitting the electron tubes being exhausted to be heated at about 450 or 500°C, in order to carry out preliminary degassing and especially to remove the water vapour absorbed on the internal walls of the bulb. As an indication, the required electric power is about 3 to 4 kW.

(d) A Tesla coil (described in Sec. 5.5.1), supplying high-frequency, high-voltage pulses, and useful for estimating the pressure in glass vessels, to find out leaks, etc.

(e) A hand blow-pipe, working with a mixture of coal gas and air (or even better of coal gas and oxygen) for sealing the tubes to the vacuum system, for sealing off the exhausted tubes, for heating quickly with a smooth flame certain elements when a long baking is not necessary, etc.

The applications of this pumping system to a certain number of particular operations will be discussed in Chap. VIII. In addition, its use for electron tube exhausting will be the subject of a special study in Vol. II, Sec. 14.3.2.

7.5. ULTRA-HIGH VACUUM PROBLEMS

7.5.1. Basic principles

Up to the last years, the lower pressures obtainable were those prevailing in conventional vacuum tubes, i.e. about 10^{-6} mm Hg. In fact, experience shows that the grid inverse currents due to ioniza-

tion phenomena which subsist in these tubes at these pressures (10^{-7} A) are low enough not to disturb the operation of the equipment using these tubes.

However, for some years it has become necessary in some cases to obtain very much lower pressures, i.e. ranging from 10^{-6} to 10^{-12} mm Hg.

The general principles which rule the design of ultra-high vacuum devices may be summarized as follows:

1. Complete elimination of rubber gaskets and use of sealed joints.
2. Use of envelope materials having very low permeability to atmospheric gases: borosilicate glass, copper, nickel, molybdenum or stainless steel.
3. High temperature baking-out of the container to be exhausted, and also of the components which connect it to the vacuum system: gauges, cold traps, valves, etc.
4. Use of diffusion pumps provided with efficient cold traps, or better, use of titanium pumps (see Sec. 5.1.3.5).

As examples, we shall tell how these problems are presently solved in two different applications: low noise, long life, high voltage electron tubes on one hand, thermonuclear fusion experimental devices on the other.

7.5.2. Ultra-high vacuum pumping systems for special electron tubes

Certain microwave tubes (travelling-wave tubes, klystrons, see Vol. II, Chap. 9) are very sensitive to the presence of residual molecules which increase the noise† widely. This phenomenon occurs because in these tubes electrons are gathered in a high density, high energy beam which exhibits many more ionization properties than that of scattered electron flows.

The same problem of pressure lowering occurs for very long life electron tubes, in which gas streaks may poison the cathode slowly.

At last, tubes using high voltages require very low pressures in order to avoid risks of electrical breakdown.

As a matter of fact, using a good getter and especially a combination of getters (e.g. barium + titanium), pressures as low as 10^{-8} or 10^{-9} mm Hg can be produced into the bulb of the tube at least in the

† This name is given to spurious random currents which add to the principal signal and disturb it. This problem will be handled in Vol. II, Appendix V.

beginning of the life. But if particular precautions are not taken, gases will be more or less rapidly released from the electrodes or from the bulb walls.

Then, in addition to careful choice of the materials of which the envelope is made, as we said above, we ought to carry out the pumping with special attention.†

There is obviously a great advantage in baking out the tube at the beginning of the pumping, at the highest possible temperature. But limitations occur from the bulb softening when it is made of glass, or from the porosity of hard materials such as metal or ceramic.

A substantial improvement is obtained by using a pumping system which applies vacuum at the same time inside and outside the tube (see Fig. 7.24).

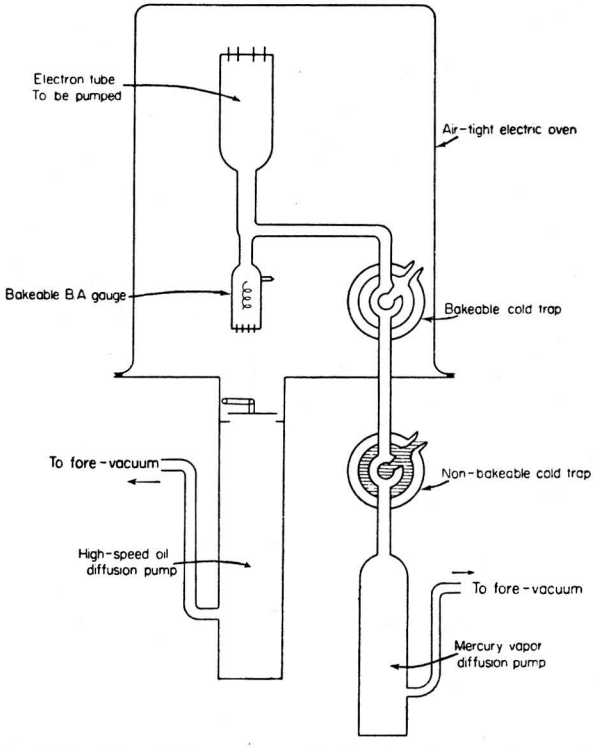


FIG. 7.24. Ultra-high vacuum double circuit pumping system.

† The pumping of conventional tubes will be described in detail in Vol. II, Sec. 14.3.

Thanks to this method:

1. Glass does not suffer mechanical stresses from atmospheric pressure, and therefore is prevented from getting squeezed, and,

2. With other material, even porous when hot, air does not enter the tube.

This feature, in conjunction with the basic principles stated in Sec. 7.5.1, permits bake-out temperatures of about 600°C with borosilicate glasses, and 800°C with hard materials. Vacua of the order of 10^{-9} to 10^{-10} mm Hg may be obtained in electron tubes so pumped.

7.5.3. **Pumping systems for thermonuclear devices**

At the present time, all over the world physicists are endeavouring to make heavy hydrogen atoms undergo nuclear "fusion", in order to produce energy by the disappearance of matter. This "thermonuclear" reaction requires the use of gases having an extremely high degree of purity. For that reason, it is necessary to degas carefully the container in which the reaction takes place, and to achieve vacua of at least 10^{-10} mm Hg, before heavy hydrogen is introduced.

The pump is usually a high speed oil diffusion pump followed by one or several efficient liquid air traps.

The container is generally made of stainless steel, and is connected to the pumping system by metallic tubes and demountable knife-edge seals (see Sec. 7.3.1.2). During pumping, it is baked for many days at 500°C.

CHAPTER VIII

PHYSICAL-CHEMICAL TECHNIQUES USED IN ELECTRON TUBE MANUFACTURE

In this chapter we shall study some procedures commonly used in electron tube manufacture and involving changes of state, surface reactions, chemical combinations or electrical phenomena.

8.1. COATING OF SOLID SUBSTANCES BY EVAPORATION IN VACUUM

8.1.1. Generalities

The technique for the evaporation in vacuum of various products (especially of metals) is very much used not only in electron tube manufacture, but also in optics and even recently for the ornamentation of various objects.

The advantages of this procedure compared with other coating methods (painting, electrolysis) are the following:

(a) Owing to the suppression of oxidation, perfectly bright and clean coats are obtained.

(b) These coatings may be excessively thin, which is especially valuable in electron devices, because, whilst keeping the electrical properties of a bulk metal (conductivity, screening effect) electrodes may be obtained using only a very small quantity of material, which makes outgassing very easy.

(c) By these means, some metal layers may be coated on insulating supports (glass or mica).

On the other hand, this procedure cannot be easily applied to the coating of surfaces with a non-flat shape, such as wires, grids, etc.

To evaporate a material in vacuum, the following principles have to be taken into account:

(a) The mean free path in the vessel in which the operation is carried out must be high in relation to the distance between the evaporating source and the object to be coated. If this were not done, there

would be many collisions of the evaporated molecules against those of the residual gas. The result would be chemical reactions and the formation of a coating which is lustreless and dirty.

(b) The evaporated atoms move along straight paths; so, any interposition of an object producing a shadow must be avoided. On the contrary, masks will be set in front of the areas which must not be coated.

(c) The thickness of the layer obtained is in inverse ratio to the square of the distance between the source and the object to be coated.

8.1.2. The apparatus employed

Evaporation is carried out in a demountable glass or metal bell-jar (in the latter case, the bell-jar is provided with a glass window enabling one to watch the operation, Fig. 8.1).

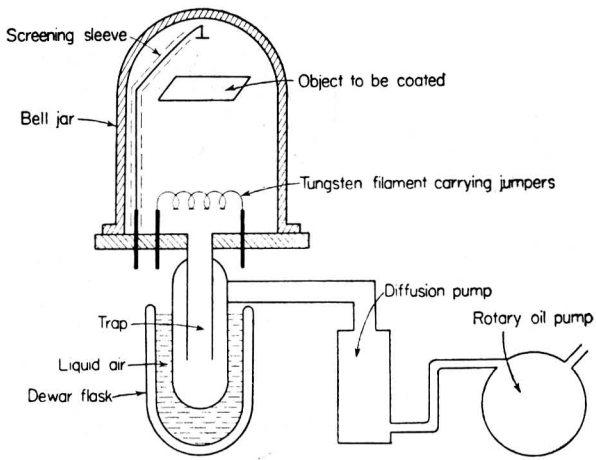


FIG. 8.1

The bell-jar sits on a ground and greased base or is provided with a circular and greased rubber gasket ensuring air-tightness. The linear dimensions of the bell-jar being about 50 cm to 1 m, the necessity for a large mean free path, compared with the path of the molecules to be deposited, necessitates a vacuum of about 10^{-5} mm Hg. This will be obtained with a system employing a vane-type pump backing a diffusion pump followed by a liquid air trap. The latter is compulsory if a mercury diffusion pump is used, but may be removed for work

with an oil pump. However, even in this last case, the trap is required in the manufacture of photocells and their derivatives (see Vol. II, Sec. 15.2).

To evaporate the chosen metal, a tungsten filament heated by Joule effect is used. Tungsten is peculiarly convenient for that use, because its vapour pressure at 2600°K is only 10^{-6} mm Hg. It then allows the evaporation of any other metal.

8.1.3. The method of operation

The tungsten filament, being formed in the shape of a horizontal spiral, is connected to a heating transformer. The metal to be evaporated is cut into small wires of a few mm length and put as jumpers upon each turn of the filament (Fig. 8.1).

Then, with the object to be coated out of the way, the bell-jar is closed and a good vacuum is achieved ($\sim 10^{-5}$ mm Hg). The filament is then gradually heated a little above the melting temperature of the jumpers. They melt and the metal "wets" the tungsten and is gathered as very adhesive drops.

Then the filament is cooled down, the bell-jar is opened and the article to be coated is placed in it.

It will previously have been carefully cleaned. For instance, it may be immersed for 2 hr in mixed sulphuric and chromic acid (50 + 50), then washed with distilled water and finally dried in a dust-free atmosphere. Optical glasses are preferably prepared by polishing them with a cotton-wool plug smeared with a paste of calcium carbonate; then they are washed and dried.

After the object has been set in place in the bell-jar, a further cleaning is done, but this time by means of an electrical discharge in a gaseous atmosphere. For that, only a partial vacuum is achieved, by isolating the bell-jar when the pressure reaches 10^{-1} to 10^{-2} mm. A potential difference of some thousands of volts is applied between the filament (switched-off) and an auxiliary electrode put for that purpose at the top of the bell-jar. Then the object to be coated is immersed in the glow discharge which occurs, and it is likely that the ion bombardment to which it is subjected eliminates all the impurities located on the surface.

After about 15 min, the discharge is cut off and the vacuum brought down to about 10^{-5} mm. The filament is then heated in order to pro-

ceed with the evaporation of the metal: it lasts from several seconds to a few minutes, according to the required thickness and the temperature reached. As an indication, when the vapour pressure of the material reaches 10^{-2} mm Hg, the coating occurs visibly (see Table 4.1).

When necessary, this thickness may be controlled with the help of a light beam passing through the object (if it is naturally transparent), and then falling upon a photocell. It is also possible to calculate the total weight of the metal to be put on the filament and to be entirely evaporated in order to obtain a certain thickness upon the object. This weight will be found to be given by:

$$P \sim 4\pi R^2 e d$$

with:

R = filament-to-object distance,†

d = density of the metal,

e = thickness of the layer.

8.1.4. **The metals which can be evaporated**

Aluminium is very often used, in electron devices as well as in optics, because it enables one to obtain remarkably adhesive, very bright and very good electrically conductive layers which are self-protecting from atmospheric agents. As further examples, it may be mentioned that very good results are also obtained with silver, gold, nickel and copper.

8.1.5. **Evaporation of solid non-metallic materials**

The same system allows one to deposit non-metallic materials, for instance lithium and calcium fluoride used for the manufacture of photographic lenses, or even sulphides and oxides of lead, cadmium, etc., used in photo-electricity.

In these cases, the material is reduced to powder and a paste is made with amyl acetate and a little nitro-cellulose as a binder: the tungsten filament is covered with this paste by dipping and drying. A first slight heating under vacuum, in the absence of the object to be

† This formula is only approximate because:
(a) The surface of a sphere of radius R is taken as the plane of the object to be coated.
(b) The source is neither isotropic nor a point.
(c) The density of very thin layers is different from that of the bulk metal.

coated, gives off the nitro-cellulose and allows the product to melt and adhere. The device is then ready for evaporation.

The tungsten filament may also be changed for a boat made of a folded molybdenum ribbon containing powder (Fig. 8.2).

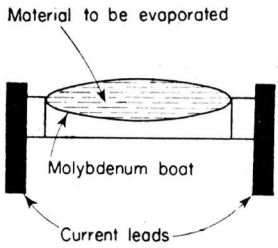


FIG. 8.2

8.2. MOLECULAR DISTILLATION

When one wants to refine products by fractional distillation, it is very useful to operate under a high vacuum: this allows one to work at much lower temperatures while avoiding reactions with atmospheric agents.

In vacuum technique, the apparatus of Fig. 8.3 enables us to refine mercury used in diffusion pumps and in gas-filled tubes (phanotrons, thyratrons, etc.).†

It comprises a glass bulb *B* containing the mercury to be refined. The mercury vapour is condensed in the cooled sloping tube *T*. The

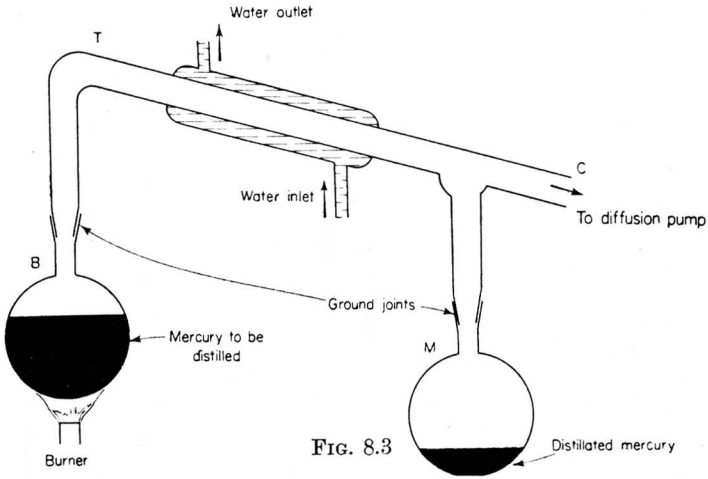


FIG. 8.3

† Before distillation, mercury must be cleaned as follows:

(a) Degreasing with an organic solvent (stir mercury in a jar containing some trichlorethylene). Decant and slightly heat.

(b) Filter on a wash-leather (by squeezing).

(c) Stir in a jar containing nitric acid diluted to 33%.

(d) Carefully wash with pure water and dry.

After these operations, mercury should not make any deposit on a clean glass plate.

whole is exhausted with a mercury diffusion pump at *C*. The refined mercury is collected in *M*.

Molecular distillation finds a place especially in the refining of organic liquids (petroleum, for example) for which it is required to work at low temperature in order to avoid decomposition of the material. This is another subject, however.

8.3. CATHODIC SPUTTERING

It has been seen (Chap. III) that, in an electric discharge, when the cathode is bombarded by positive ions it disintegrates: every ion impact tears away one or several molecules of the metal; they evaporate and deposit on the walls of the bulb or upon any other target put in their way.

This process may be used to deposit metals with very low vapour pressures, which could be deposited only with great difficulty by evaporation in vacuum: tungsten, iridium, molybdenum, tantalum, etc. However, it may be applied to a great number of metals.

TABLE 8.1

Metal	Loss of weight (mg per ampere-hour)	Metal	Loss of weight (mg per ampere-hour)
Bi	1470	Fe	68
Te	1200	Ni	65
As	1100	W	57
Tl	1080	Co	56
Sb	890	Mo	56
Ag	740	Mn	38
Au	460	Cd	32
Pb	400	Al	29
Zn	340	Cr	27
Cu	300	Ta	16
C	262	Mg	9
Sn	196		

With metals which oxidize only slightly, such as iridium, platinum, gold, palladium, excellent results are obtained by making the discharge glow in air at a pressure lying between 0·1 and 1 mm Hg.

With oxidizable metals, hydrogen or argon can be used: Table 8.1 gives† the loss of weight of a cathode made with different metals, in

† From A. Guntherschulze, *Z. Phys.* **36**, 563 (1926).

mg per ampere-hour, the pressure being adjusted so that the voltage fall between the anode and the cathode should be 700 V and the current 7 mA, the gas in which the discharge occurs being hydrogen.

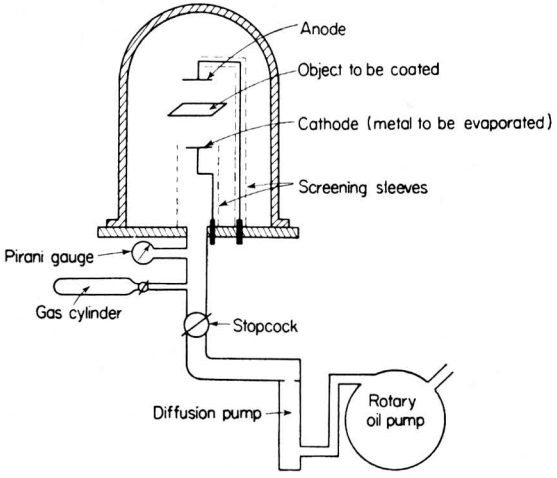


FIG. 8.4

The system will include (Fig. 8.4) a bell-jar, a vane-type pump, a diffusion pump, a Pirani gauge; and a system for the inlet of gases has to be provided.

If the discharge occurs in air, only the vane-type pump is necessary. In the other case, before the admission of the gas, it is necessary to obtain a vacuum as good as possible with the diffusion pump.

An example of the application of this procedure is the deposition of a conducting, semi-transparent iridium layer on the glass windows on which the photocathodes of television camera tubes are formed (see Vol. II, Sec. 15.3).

8.4. DEGASSING OF METALS

It has been seen (Chap. IV) that various materials used in vacuum technique fix considerable quantities of gases, either by plain adsorption (glass, mica), or by a combination of adsorption, chemisorption and solid solution (metals).

Release of these gases during pumping is essential for the electron tube manufacturer, failing which the pressure in the tubes would increase more or less quickly during their life.

Desorption (or degassing, as it is currently called) is usually achieved in two stages.

8.4.1. **Preliminary stoving of metal parts in vacuum or in hydrogen**

The phenomena of the fixing of gases by metals, as seen in Chap. IV, are rather slow procedures requiring times of the order of 1 hr.

It is then advantageous to proceed to a first degassing of the parts before the mounting, in order to avoid having too large quantities of gases to remove† during the tube exhausting.

This stoving is practised either in a vacuum or in a hydrogen stove. In both cases, the temperature must reach 900 to 1000°C and the stoving time must lie between 10 min and 1 hr, according to the volume of the parts.

8.4.1.1. *Stoving in Vacuum*

This is a very efficient process, with the condition that the parts so treated are either stored under a good vacuum (for instance in sealed

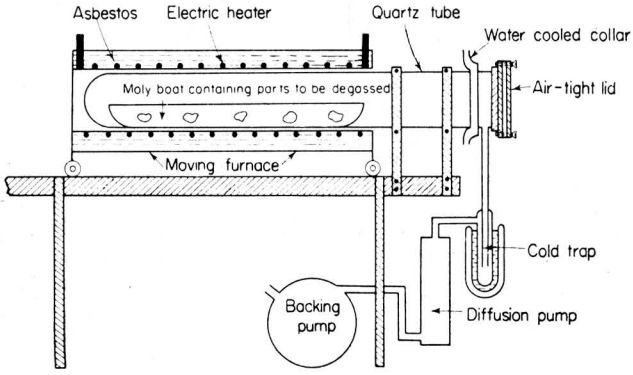


FIG. 8.5

bulbs), or assembled and very quickly pumped after stoving: this is because a metal heated in vacuum offers a very high absorption effiency for atmospheric gases.

Figure 8.5 represents such a type of a stove. Pressure must be brought down at least to 10^{-3} mm, in order to avoid the oxidation of the treated parts.

† By being released in too large quantities in the bulb, these gases could poison the cathode.

In a laboratory, when it is required to treat only a small number of small size pieces, they may simply be placed in a small cylindrical molybdenum boat, put under a vacuum bell-jar and heated from outside by h.f. induction (see Sec. 8.4.2.2).

8.4.1.2. *Stoving in Hydrogen or in Forming-gas*

In the electron tube industry, this process is more commonly used than stoving under vacuum, because the following advantages are obtained:

Since it happens in a gas at atmospheric pressure, it avoids the necessity of obtaining a very good vacuum, which is not always easy to get when a great number of parts have to be treated at the same time (dimensions of the stove, leaks, etc.).

The components processed in hydrogen are cleaned of the other gases (especially oxygen and oxides are changed into water vapour which is driven out). After which, the pores of the metal being saturated with hydrogen, further absorption power for atmospheric gases is greatly reduced, which allows one to leave the parts exposed to air for a longer time before using them.† As for hydrogen, it has been seen in Chap. IV that it is very easily removed during pumping.

With pure hydrogen one runs the risk of explosion, and it is better to use a mixture of 75% H_2 and 25% N_2, obtained by the dissociation of ammonia. This mixture is called "forming-gas" or "mixed gas" and is marketed in metal cylinders at a pressure of 150 kg/cm².

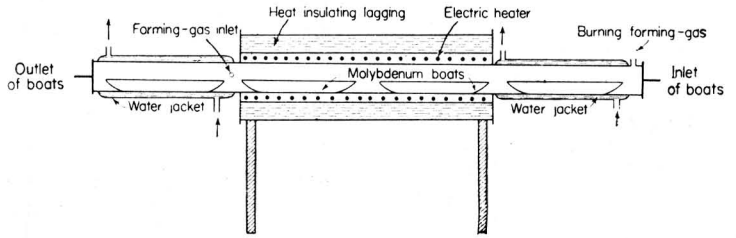


FIG. 8.6

Figure 8.6 represents a hydrogen or forming-gas stove for continuous working. The apparatus consists of a tube made of a refractory material. It is heated by a nickel-chromium resistor consuming 3 to

† However, it is necessary not to exceed a storage time, to air exposure, of 24 hr for large-size parts, such as anodes for instance.

4 kW, and covered with a thick asbestos layer for heat insulation. The stove has 3 parts: the central part which is the only one heated and the ends which are cooled by a water-jacket of roughly 50 cm in length. Forming-gas inserted near the centre at a flow of about 5 l./min, is burned at one end in order to avoid the formation in the workshop of an explosive mixture. Two doors allow us to insert at one end and to extract at the other the molybdenum boats containing the pieces to be stoved. At each insertion of a boat, another boat which has been treated and then cooled at the refrigerated end is taken away.†

8.4.2. **Degassing during pumping**

Preliminary stoving under vacuum or under forming-gas is not sufficient to degas the parts entirely, more especially when these are exposed to air for a certain time before pumping.

This is why the final degassing is done during the pumping of the electron tube.

8.4.2.1. *Baking*

With the tube connected to the diffusion pump, it is covered by a gas or an electric oven. The temperature is raised to the highest value which avoids the softening of the glass of the bulb, say about 400°C for lime glass and crystal glass, 450°C for MO glass, 500°C for Pyrex and other glasses of the same kind.‡

In principle, this operation aims at removing gases and water vapour absorbed on the internal surface of the bulb and of the insulators (micas, ceramics), and in this case, a baking time of 15 to 60 min is enough.

On the other hand, in specific cases, when h.f. heating of the electrodes is impossible,§ the baking also aims at degassing the electrodes and the metallic parts. It is then necessary to extend the baking to several hours.

† In a laboratory, small quantities of parts may be treated by placing them in a molybdenum crucible covered by a glass bell-jar. Forming-gas is allowed to flow inside the bell-jar and the crucible is heated by induction.

‡ These various kinds of glasses will be studied in Vol. II, Sec. 14.2.

§ This is the case of photocells, television camera tubes and generally of all tubes including non-bulk electrodes. Heating by h.f. must also be avoided in tubes using an electron-optical structure requiring strict mechanical accuracy.

8.4.2.2. *Induction Heating by High frequency Currents*

In the most general case, baking is followed by a strong degassing of the electrodes, obtained by surrounding the tube bulb with a solenoid made of large diameter copper wire carrying a h.f. current.

The anode, the grids, and generally the metallic electrodes included in the bulb are submitted to Eddy current heating.

The arrangement of the solenoid varies according to whether the purpose is to heat cylindrical electrodes or flat ones, or to "flash" a getter, etc. (Fig. 8.7).

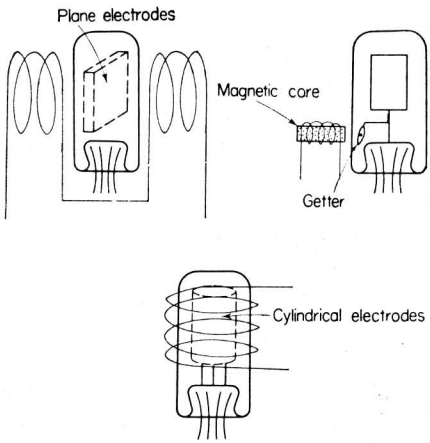


FIG. 8.7

In the case of nickel, the optimum temperature reached during the h.f. heating is about 800 to 1000°C. Below that, the degassing would not be sufficient; above that temperature, the metal would begin to evaporate, which generally involves a contamination of the cathode and a decrease of the insulation of the spacers because of the conductive coating formed on their surfaces.

The generators used are in most cases triode oscillators. The design of the oscillating circuit must be such that the oscillation conditions of the triode are not disturbed by the load variations on the oscillating circuit. A commonly used diagram is given in Fig. 8.8.

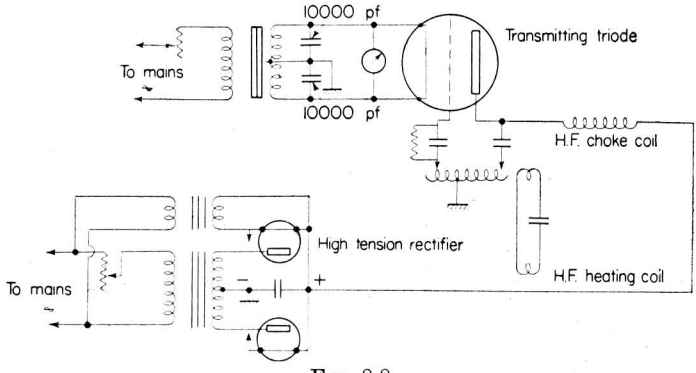


FIG. 8.8

A careful filtering of the anode voltage is not compulsory. The chosen frequency lies between 300 and 500 kHz.† For high powers, the heating coil must be made of a water-cooled copper tube.

The power required to heat to a temperature T an electrode having a lateral surface S is obtained by applying the Stefan–Boltzmann formula:

$$P = 5{\cdot}7\times10^{-12}\times S\times\varepsilon_t\times T^4 \text{ (watts, cm}^2\text{, °K)}.$$

ε_t is the total emissivity of the metal forming the electrode.‡ The number of ampere turns of the heating coil can be deduced by applying the following formula:§

$$N\,I = \sqrt{\left(\frac{P}{2{\cdot}8\times10^{-4}\times K\times(F\times\varrho)^{1/2}}\right)}$$

in which:

N = is the number of turns of the coil,
I = the current traversing it, in amperes,
F = the frequency of this current, in cycles per second,
ϱ = the hot resistivity of the metal forming the electrode, in $\Omega\times$cm,
K = a parameter depending both on D/d and d/h where:
D = the diameter of the heating coil,
d = the diameter of the electrode to be heated,
h = the height of this electrode.

Table 8.2 gives the values of K for some values of D/d and of d/h.

TABLE 8.2

D/d	d/h	K
1·2	1	1·6
	0·5	0·9
	0·2	0·4
1·8	1	0·9
	0·5	0·7
	0·2	0·3

† Government laws fix the frequency ranges to be used, the maximum interference fields produced in the neighbourhood of the apparatus, etc.

‡ If the accurate value of ε_t is unknown, there will not be a large error in taking $\varepsilon_t = 0{\cdot}3$ for a metal with a clean surface, and 0·8 for an oxidized or blackened surface.

§ Reche, Wiss, Veroff, Siemens Konz. 1, quoted by J. Yarwood (5).

EXAMPLE: An anode of a 6V6 tube is to be heated to 900°C; it has nearly the shape of a blackened nickel cylinder of about 3 cm height and 3 cm diameter. The resistivity of nickel at 900°C is 45 $\mu\Omega$ cm.

The required power is:

$$P = 28 \times 0{\cdot}8 \times 5{\cdot}7 \times 10^{-12} \times (1173)^4 = 279 \text{ W}.\dagger$$

If a coil of 5 cm diameter is used, Table 8.2 gives for K the value 0·9. In addition, if the oscillator frequency is 500 kHz, one obtains:

$$NI = \sqrt{\left(\frac{270}{2{\cdot}8 \times 10^{-2} \times 0{\cdot}9 \times (5 \times 10^5 \times 45 \times 10^{-6})^{1/2}}\right)} = 475$$

so that with a coil having 8 turns, an h.f. current of 60 A r.m.s. would be necessary.

8.5. GAS ANALYSIS

It is very often required to know the nature and the proportions of the gases dissolved in a metal. It may also be required to obtain similar information about unwanted gases causing trouble in the proper operation of certain electron tubes.

Analysis operations may be done in several ways.

8.5.1. **Physical-chemical analysis**

Figure 8.9 gives a schematic diagram of the procedure devised by Langmuir.

The pieces of the metal to be analysed are placed in a quartz tube connected to a system comprising essentially an oil diffusion pump and a McLeod gauge. For simplicity, the metal will be assumed to contain only the following gases: H_2O, CO_2, O_2, CO, H_2, N_2.

At the beginning of the operation the taps R_1 and R_2 are opened.

When as good a vacuum as possible is obtained (10^{-5} to 10^{-6} mm Hg), the tap R_1 is closed, and the sample of metal is heated by means of a small electric stove to allow the gases to escape (temperature: 800 to 1500°C, according to metals).

† Owing to the generally bad matching of the load, an efficiency higher than 0·3 is not to be expected. It is then necessary to have a generator consuming from the mains about 1 kW for each electron tube to be degassed, say about 10 kW for an automatic turntable pump having 10 positions of heating (see Vol. II, Sec. 14.3.3).

The new pressure is then measured. Knowing the total volume of the system, the total quantity of gas released by the metal can be deduced.

After which, the tap R_2 is also closed.

The side tube 1 is then cooled by a mixture of dry ice and acetone (−78°C). Thus the water vapour contained in the gas is condensed; the pressure variation gives the proportion of H_2O.

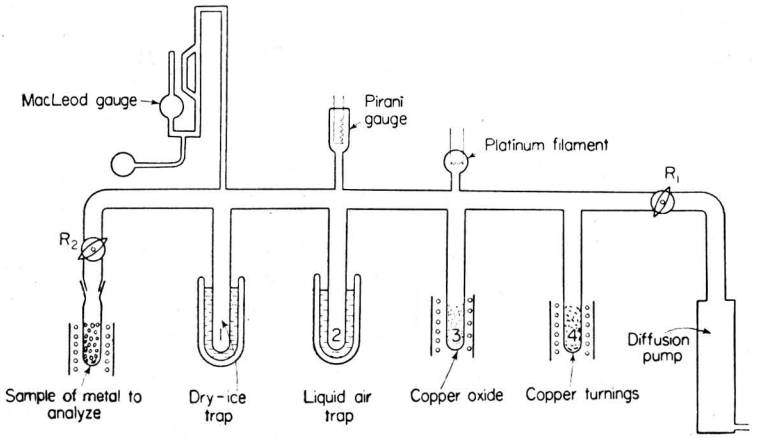


FIG. 8.9

Then the side tube 2 is cooled by liquid air, which condenses CO_2. A new measurement of the pressure allows the quantity of CO_2 to be calculated.

To determine the oxygen, an attempt is made to react this with any hydrogen which may be present by heating a platinum filament. The water vapour formed is estimated as above, by condensation with dry ice.

It is to be mentioned that during this operation the CO present in the system is changed into CO_2. The latter is determined, as stated above, by condensation with liquid air.

After that, according to whether the remaining gas contains oxygen or hydrogen (or still CO), one proceeds to fix the first by heating to 800°C the side tube 4 which contains copper turnings, or to oxidize the other two, by heating the side tube 3 which contains cupric oxide.

Again the H_2O or CO_2 produced estimated. Finally, the gas resisting all the above operations is deemed to be nitrogen.

8.5.2. **Mass spectrograph analysis**

In Vol. II (Sec. 5.2), it will be seen that when a particle with a mass m and a charge e is submitted to a magnetic field H, normal to its path, the latter assumes a radius of curvature:

$$R = \frac{1}{H}\sqrt{\left(\frac{2\,m\,V}{e}\right)}$$

(V being the acceleration voltage of the particle). This gives a method of separating particles of different masses.

A mass spectrograph (Fig. 8.10) comprises a filament emitting electrons and an electrode collecting them. Gaseous molecules are injected in the path of the electrons and are ionized. The ions produced are focused and accelerated. The ion beam is deflected by a magnetic field, and collected by a final electrode, masked by a screen provided with a slit. Only the ions for which the various parameters fulfil the above relation will be collected. The current flow producing the magnetic field may then be calibrated in terms of atomic masses.

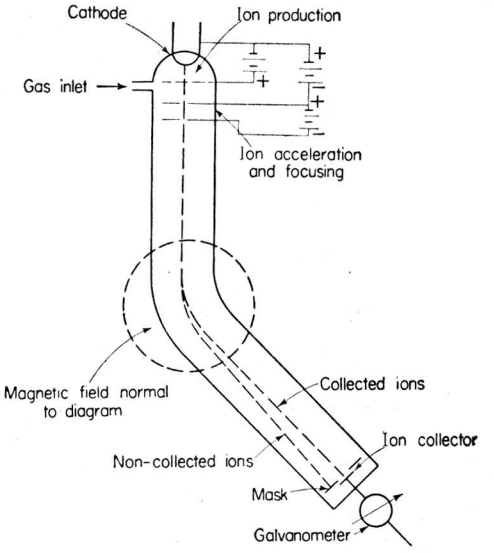


FIG. 8.10

On the other hand, the proportion of each kind of ion is given by the relative values of the collected current.

This system has great accuracy and an excellent sensitivity, but suffers from the disadvantage of being very expensive.

8.5.3. Analysis by an optical spectrograph

It has been seen in Chap. III (Sec. 3.8), that the light emitted by an ionized gas shows "discrete" frequencies corresponding to the different excitation and ionization levels of the gas in question. The entirety of these frequencies which is very characteristic of this gas, is known as the "line spectrum". It is exhibited with the help of a prism spectrograph, using the general property of prisms to deviate light all the greater as its wave-length is smaller (Fig. 8.11).

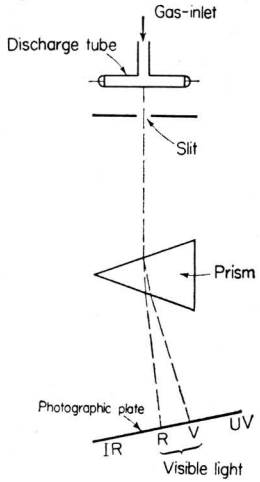


FIG. 8.11

A glow discharge is then excited in the gas to be analysed. The light emitted passes through a slit diaphragm, the beam is then resolved by a glass or quartz prism and the spectrum obtained is received on a photographic plate.†

The study of this spectrogram will enable us to determine qualitatively (and with less accuracy, quantitatively), the nature of a gaseous mixture. This work, however, can only be done by specialists.

8.6. INTRODUCTION OF GAS IN A VACUUM SYSTEM

It is frequently necessary to admit into a pumping system specific gases at determined pressures, for example, in the following cases:

To obtain a metallic coating by cathodic sputtering;

To clean a surface by ion bombardment;

To manufacture gas-filled tubes, etc.

8.6.1. Production of gases

To obtain very pure gases, it is best to buy them in glass bulbs of volume about one 1 l., filled with the desired gases at atmospheric pressure. Whilst it is possible to produce the common gases (H_2, O_2, N_2) by physical-chemical procedures, the purchase of pure gases in glass bulbs is the only way to obtain inert gases when required.

† A calibrated photocell may also be moved along the spectrum.

The bulbs are supplied by the maker with a sealed-off tip which is extended by a glass tube to be connected to the system after an iron slug has been inserted. When it is required to extract the gas from the bulb, the slug is lifted with a magnet and is allowed to fall on the sealed-off tip ending the bulb, and break it (Fig. 8.12).

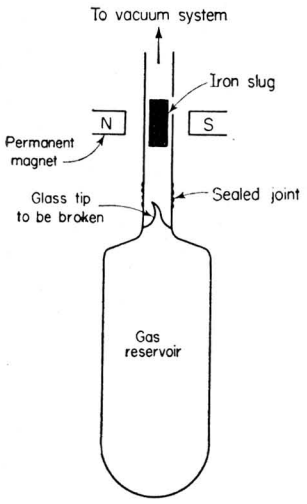


FIG. 8.12

On the other hand, it is easy to produce pure oxygen by carefully heating a glass tube connected to the system and containing potassium permanganate (Fig.8.13).

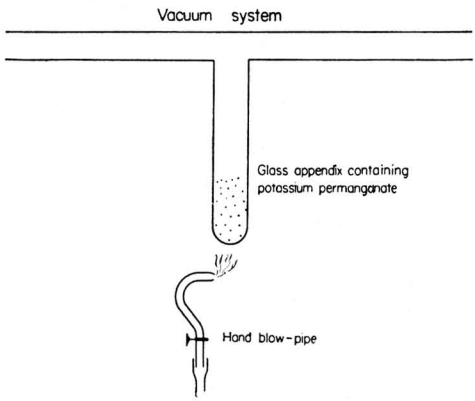


FIG. 8.13

It is also possible to obtain hydrogen by the action of dilute hydrochloric acid on aluminium, carbon dioxide by action of the same acid on calcium carbonate, nitrogen by gentle heating of ammonium nitrite, etc. Lastly it is possible to use compressed gases sold in metal cylinders at 150 kg/cm^2, but with no guarantee of purity.

In these cases, as in chemical processes, the gases must be purified.

8.6.2. **Purification of gases**

It is necessary to start by removing water vapour which generally constitutes the most important impurity: for that purpose, the gas is bubbled through concentrated sulphuric acid, and then passed into a tube containing caustic potash in small pieces or calcium chloride.

Then, in the case of hydrogen, nitrogen and carbon dioxide, the traces of oxygen must be eliminated. For this purpose, the gas passes

through copper turnings heated at 800°C. With hydrogen, this operation releases water vapour which is removed by a further passage through caustic potash (or P_2O_5).

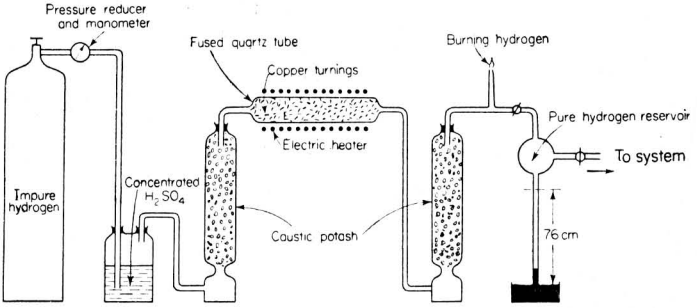


FIG. 8.14

After purification, the gas is stored in a reservoir provided with a mercury manometer, whilst extra gas is released to the atmosphere. With hydrogen, the release to atmosphere is avoided by igniting it at the outlet of a nozzle† (Fig. 8.14).

8.6.3. **Introduction of gases**

The pressures of the gases used are usually between 10^{-3} and 760 mm Hg. This range is largely the field of the McLeod gauge. However, as this gauge does not have a continuous reading, it is generally rejected because it would require many trials to obtain the desired pressure accurately.

This is the reason why it is usually better to use:

From 10 to 760 mm: the mercury manometer,

From 0·1 to 10 mm: the oil manometer,

Below 0·1 mm: the Pirani gauge.

The introduction of gas into a system often requires an accurate control which may be obtained with a needle valve described in Sec. 7.3.2.

In the case of hydrogen, the porosity of palladium to this gas may be used: a tube of this metal, having thin walls (0·2 mm) is closed at

† At the beginning of the operation a mixture of hydrogen and air comes out at the nozzle. If it were pre-ignited, it would cause the explosion of the reservoir; to avoid this, a little gas is collected in a upturned test-tube and is ignited at a certain distance: it is only when this ignition occurs without explosion that hydrogen may be ignited at the nozzle.

one end and connected at the other end to the pipe supplying the hydrogen. By heating the palladium (for instance with the help of an electrical heater), the hydrogen flow may be accurately controlled (Fig. 8.15).

A similar system may be employed for oxygen by using a silver tube; likewise nitrogen and carbon dioxide may be controlled with the help of an iron tube.

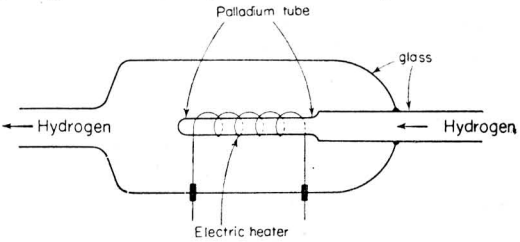


FIG. 8.15

8.7. LEAK FINDING

The problem of leak finding is often a real bugbear for vacuum technicians. Two cases may be distinguished according as we are concerned with leaks on a pumping system or on a sealed electron tube, but only the first case will be studied here; the second one will be examined in Vol. II.

8.7.1. **Primary methods**

If the pressure in a given system does not fall to a value as low as attainable in principle by the apparatus (about 10^{-3} mm Hg for a mercury diffusion pump without a trap, about 10^{-6} for the same pump with a liquid air trap, or for an oil diffusion pump), the following tests may be made:

(a) Check first that all the movable joints (taps, ground-joints, etc.) are truly vacuum-tight: it often happens that badly greased taps are prone to leak. Check also that the fore-vacuum is sufficient to back the diffusion pump.

(b) If the leak is so large that a purple ionization occurs with the antenna of the h.f. Tesla coil (see Sec. 6.5.1), try to find the crack (invisible to the naked eye) by slowly moving the antenna along the glass tubes. With large leaks and a little luck, it is possible to see the discharge focusing at the place of the crack in the shape of a bright point. This procedure does not apply of course to metallic pipes or glass-to-metal seals.

(c) If this test is not successful, connect the Tesla coil to the discharge tube and let it work permanently. Then, with the help of a

brush, slowly and systematically spread alcohol over the different parts of the system: if alcohol is sucked into the crack, the ionization glow of the discharge tube is changed from purple to a blue colour.

(d) If this does not work, and if electron tubes are being pumped on the system, take them away one after the other: one of them may be responsible for the leak.

(e) If there are any picein joints, melt them again to eliminate any cracks which may be inside.

(f) Finally, one may suspect poor working of the diffusion pump (which may often get contaminated), and also a lack of pumping fluid or of heating power.

8.7.2. **Improved methods**

8.7.2.1. *The mass spectrograph*

A mass spectrograph (see Sec. 8.5.2) is connected to the faulty system. Then, along the suspected components, a nozzle is carried from which issues a low flow (about 1 l./min) of a light gas contained in air in only small proportions (hydrogen or helium). The spectrograph has been previously adjusted for the molecular mass of this gas, so that as soon as the gas jet reaches the leak, the indicator of the spectrograph deviates.

Unfortunately, the mass spectrograph is a very expensive apparatus, which may often be replaced by the following devices.

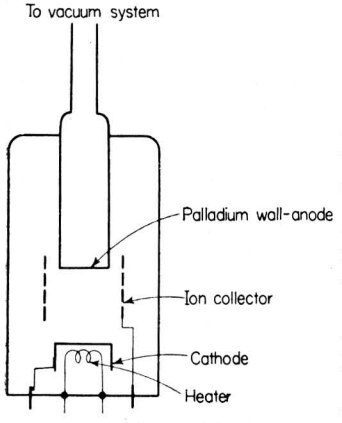


FIG. 8.16

8.7.2.2. *The R. C. A. palladium wall gauge*

This is an ionization gauge, the bulb of which is divided into two chambers by a thin palladium wall. This separating wall is also used as the anode of a triode placed in the lower chamber in which a good vacuum is achieved (Fig. 8.16). As for the upper chamber, this is connected to the system to be checked.

When the triode is working, the anode heated at about 800°C by electron bombardment becomes pervious to hydrogen, exclusive of other gases. It is then sufficient to carry a hydrogen jet along the

suspected parts: as soon as it passes over the leak, the microammeter measuring the ion current is observed to deviate.

Of course, when the leak has been detected, the anode must be kept heated for a few minutes in order to remove hydrogen from the main chamber.†

8.7.2.3. *The halogen leak detector*

This device uses the property, shown by heated platinum, to emit positive ions from alkali compounds present as impurities. This property is very much increased in an atmosphere containing chlorine.

The detector comprises a platinum filament diode, connected to the system in which the leak has to be found. The filament is heated at about 1000°C and the anode taken to a negative voltage of a 100 V with respect to the filament. Along the suspected parts of the system one carries a nozzle from which issues a small freon jet (CCl_2F_2). The presence of the leak is checked by a sudden deflection of the milliammeter in the diode circuit.

8.7.2.4. *Other devices*

A Pirani gauge with a hydrogen jet may be used. Hydrogen being a better heat conductor than air, it produces a current increase in the gauge galvanometer.

Further, two ionization gauges may be mounted as a Wheatstone bridge, one of them being connected to the system through a liquid air trap. The leak is investigated with the help of an easily condensable gas (CO_2 for instance). The gas is stopped by the liquid air trap for one of the gauges, whilst it reaches the second one. The bridge balance is then upset.

A silica gel leak detector was recently designed at Philips Laboratories. Air entering the crack is stopped by a trap using silica gel cooled by liquid-air. On the other hand, helium used for leak finding easily passes through the trap.

† This gauge type number 1945, has the following electrical characteristics: $V_F = 6{\cdot}3$ V, $V_a = 185$ V, $I_a = 32$ mA. Ion collector voltage $= -22$ V. A getter, heated by Joule effect, is provided in case a good vacuum cannot be obtained again in the gauge.

APPENDIX I

COMMON PHYSICAL CONSTANTS

Velocity of light	c	$= 2{\cdot}9978 \times 10^{8}$ m sec^{-1}
Electronic charge	e	$= 1{\cdot}601 \times 10^{-19}$ C
Electronic mass	m	$= 9{\cdot}107 \times 10^{-31}$ kg
Mass of proton	M_1	$= 1{\cdot}672 \times 10^{-27}$ kg
Specific charge of electron	e/m	$= 1{\cdot}759 \times 10^{11}$ C kg^{-1}
Ratio of proton mass to electron mass	M_1/m	$= 1836$
Gas constant	R	$= 8{\cdot}314$ J (°K)$^{-1}$ mole^{-1}
Boltzmann's constant	k	$= 1{\cdot}38 \times 10^{-23}$ J (°K)$^{-1}$
Avogadro's number	N	$= 6{\cdot}025 \times 10^{23}$ mol. mole^{-1}
Planck's constant	h	$= 6{\cdot}623 \times 10^{-34}$ J · s
Stefan–Boltzmann's constant	σ	$= 5{\cdot}672 \times 10^{-12}$ W cm^{-2} (°K)$^{-4}$
Mechanical equivalent of the calorie	J	$= 4{\cdot}185$ J
Equivalent of electron volt	1 eV	$= 1{\cdot}601 \times 10^{-19}$ J

PERIODIC TABLE

Group → / ↓ Period	I a	I b	II a	II b	III b	III a	IV b	IV a
1	H 1 1·0080							
2	Li 3 6·940		Be 4 9·013			B 5 10·82		C 6 12·01
3	Na 11 22·997		Mg 12 24·32			Al 13 26·97		Si 14 28·06
4	K 19 39·096	Cu 29 63·54	Ca 20 40·08	Zn 30 65·38	Sc 21 45·10	Ga 31 69·72	Ti 22 47·90	Ge 32 72·60
5	Rb 37 85·48	Ag 47 107·880	Sr 38 87·63	Cd 48 112·41	Y 39 88·92	In 49 114·76	Zr 40 91·22	Sn 50 118·70
6	Cs 55 132·91	Au 79 197·2	Ba 56 137·36	Hg 80 200·61	Lanthanides	Tl 81 204·39	Hf 72 178·6	Pb 82 207·21
7	Fr 87 223		Ra 88 226·05		Actinides			

Lanthanides (or rare earths)	La 57 138·92	Ce 58 140·13	Pr 59 140·92	Nd 60 144·27	Pm 61 145	Sm 62 150·43

Actinides	Ac 89 227	Th 90 232·12	Pa 91 231	U 92 238·07	Np 93 237	

DIX II

OF THE ELEMENTS

V		VI		VII		VIII			0
b	a	b	a	b	a				
									He 2 4·003
	N 7 14·008		O 8 16·000		F 9 19·00				Ne 10 20·183
	P 15 30·98		S 16 32·066		Cl 17 35·457				A 18 39·944
V 23 50·95		Cr 24 52·01		Mn 25 54·93		Fe 26 55·85	Co 27 58·94	Ni 28 58·69	
	As 33 74·91		Se 34 78·96		Br 35 79·916				Kr 36 83·7
Nb 41 92·91		Mo 42 95·95		Tc 43 98·91		Ru 44 101·7	Rh 45 102·91	Pd 46 106·7	
	Sb 51 121·76		Te 52 127·61		I 53 126·91				Xe 54 131·3
Ta 73 180·88		W 74 183·92		Re 75 186·31		Os 76 190·2	Ir 77 193·1	Pt 78 195·23	
	Bi 83 209·00		Po 84 210		At 85 215				Rn 86 222

Eu 63 152·0	Gd 64 156·9	Tb 65 159·2	Dy 66 162·46	Ho 67 164·94	Er 68 167·2	Tm 69 169·4	Yb 70 173·04	Lu 71 175·0

Pu 94 239	Am 95 241	Cm 96 242	Bk 97 243	Cf 98 244	Ei 99 249	Fm 100 248		

APPENDIX III

CALCULATION OF THE MAXWELL-BOLTZMANN VELOCITY DISTRIBUTION FUNCTION

Let n be the number of molecules contained in a certain mass of gas. We shall call c the velocity of a molecule, the components of which along the three axes are respectively u, v and w.

The calculation of the distribution function uses the two essential hypotheses of the kinetic theory, viz:

(a) At any given moment there is the same number of molecules having a velocity between two given adjacent values.

(b) The gas is isotropic, which means that there is no preferred direction.

(a) *Using the first hypothesis*

We shall call $\mathrm{d}n_u/n$ the proportion of the molecules whose velocity component directed towards u is included between u and $u + \mathrm{d}u$.

It is evident that this ratio is:

On one hand, a function of the velocity component u.

On the other hand, proportional to the considered interval $\mathrm{d}u$.

It follows that:

$$\frac{\mathrm{d}n_u}{n} = f(u)\ \mathrm{d}u.$$

If we take into account the three velocity components along the three axes, we may write:†

$$\frac{\mathrm{d}n}{n} = f(u)\, f(v)\, f(w)\ \mathrm{d}u\ \mathrm{d}v\ \mathrm{d}w.$$

† In fact, we shall assume with Maxwell that they are independent one from another, the three probabilities for the velocity to have its three components included simultaneously between u and $u + \mathrm{d}u$, v and $v + \mathrm{d}v$, w and $w + \mathrm{d}w$. In such a case, the total probability is equal to the product of the three elementary probabilities.

In a way, this function gives the proportion of molecules for which the extremity of the velocity vector c (with components u, v, w) falls into a small cube having the dimension du, dv, dw (see figure).

(b) *Using the second hypothesis*

Similarly, as the gas is isotropic, it may be stated that dn/n depends only on the velocity, and not on the ratio between the components u, v and w. This may be written as:

$$\frac{dn}{n} = \varphi(c)\, du\, dv\, dw.$$

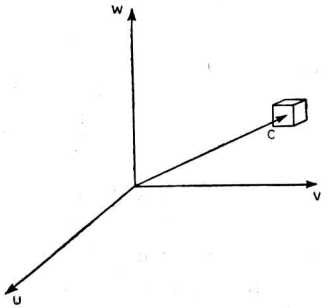


FIG. 1

As the velocity c is connected to its three components by the relation:

$$c^2 = u^2 + v^2 + w^2$$

it is then obvious that:

$$f(u)\, f(v)\, f(w) = \varphi(c) = F(u^2 + v^2 + w^2).$$

The problem amounts to finding a function $f(u)$ which fulfils this equality. Let us pass to logarithms:

$$\log f(u) + \log f(v) + \log f(w) = \log F(u^2 + v^2 + w^2).$$

Let us differentiate with regard to u, v, w:

$$\begin{aligned} d\,[\log f(u)] &= 2u\, d\,[\log F(u^2 + v^2 + w^2)]\, du, \\ d\,[\log f(v)] &= 2v\, d\,[\log F(u^2 + v^2 + w^2)]\, dv, \\ d\,[\log f(w)] &= 2w\, d\,[\log F(u^2 + v^2 + w^2)]\, dw \end{aligned}$$

from which it is deduced:

$$\frac{1}{2u}\frac{d}{du}\log f(u) = \frac{1}{2v}\frac{d}{dv}\log f(v) = \frac{1}{2w}\frac{d}{dw}\log f(w).$$

These three expressions are seen to be identically equal to a constant; in effect u, v and w being three independent variables, in order that a function of a certain variable u should be equal to the same function of another variable v for all the values of u and of v, it is necessary and sufficient that both functions should be equal to the same constant.

It follows that:

$$\mathrm{d}\,[\log f\ (u)] = 2\,u\,\mathrm{d}u \times \text{constant},$$

$$\log f(u) = A\,u^2 + B,$$

$$f(u) = a\,\mathrm{e}^{b u^2}.$$

Then, it must be obtained:

$$\frac{\mathrm{d}n}{n} = a\,\mathrm{e}^{b\,(u^2+v^2+w^2)}\,\mathrm{d}u\,\mathrm{d}v\,\mathrm{d}w.$$

Now, in this expression we may replace the velocity components u, v and w by the velocity c. The element of cubic volume $\mathrm{d}u$, $\mathrm{d}v$, $\mathrm{d}w$ may be changed into the spheric volume included between the sphere of radius c and the sphere of radius $c + \mathrm{d}c$, i.e. $4\,\pi\,c^2\,\mathrm{d}c$. Then we have:

$$\frac{\mathrm{d}n}{n} = 4\,\pi\,a\,\mathrm{e}^{b c^2}\,c^2\,\mathrm{d}c.$$

Let us now calculate the constants a and b. Concerning their sign, it is to be noted first that the probability having to be positive, a is positive. On the other hand, it is evident that the number of molecules having a certain speed must tend to zero when this speed tends to infinity. This requires that b must be negative.

To determine the values of a and b, we shall take a mass of gas equal to the molecular mass and we shall write, on the one hand, that the total number of molecules it contains is equal to the Avogadro's number N, and on the other hand, that the total energy of the molecules contained in the molecular mass is equal to $3\,RT/2$, i.e. that the average energy of a molecule is equal to $3\,RT/2\,N$, or $3\,kT/2$.

That enables us to write and to solve the two following equations:

$$\int_0^{+\infty} 4\,\pi\,N\,a\ \mathrm{e}^{-b c^2}\ c^2\,\mathrm{d}c = N.$$

and:

$$\frac{1}{2}\,m\,C^2 = \frac{m}{2\,N}\int_0^{+\infty} c^2\,\mathrm{d}n = \frac{m}{2\,N}\int_0^{+\infty} 4\,\pi\,N\,a\,\mathrm{e}^{-b c^2}\,c^4\,\mathrm{d}c = \frac{3}{2}\,k\,T$$

calling C the root mean square velocity of a gas molecule. For the calculation of the integrals, one can refer to mathematical treatises.†

† See for example: F. S. Woods, *Advanced Calculus*, Ginn and Co., 1934.

The following solutions are found:

$$\int_0^{+\infty} \mathrm{e}^{-bc^2} c^2 \,\mathrm{d}c = \frac{1}{4} \sqrt{\frac{\pi}{b^3}} ,$$

$$\int_0^{+\infty} \mathrm{e}^{-bc^2} c^4 \,\mathrm{d}c = \frac{3}{8} \sqrt{\frac{\pi}{b^5}} .$$

Then, the values obtained for the constants a and b are:

$$a = \sqrt{\left(\frac{m^3}{8\,\pi^3\,k^3\,T^3}\right)} ,$$

$$b = \frac{m}{2\,k\,T} .$$

The velocity distribution function then becomes:

$$\frac{\mathrm{d}n}{\mathrm{d}c} = n \sqrt{\left(\frac{2\,m^3}{\pi\,k^3\,T^3}\right)} \mathrm{e}^{-\frac{mc^2}{2kT}} c^2 .$$

REFERENCES

(1) G. A. Boutry, *Cours de Physique appliquée aux industries du vide.* C. N. A. M. Éditions Riber, Paris.
(2) L. Dunoyer, *Technique du vide.* Collection "Que sais-je ?", Presses Universitaires de France, Paris.
(3) S. Dushman, *Scientific foundations of vacuum technique.* John Wiley and Sons, New York.
(4) P. Fleury et J. P. Mathieu, *Physique générale et expérimentale.* Éditions Eyrolles, Paris.
(5) J. Yarwood, *High vacuum technique.* Chapman and Hall, London.

PROBLEMS

CHAPTER I

1. (A) Calculate the linear expansion of a nickel cylindrical cathode, between 20 and 750°C. The length when cold is 48 mm. Use a second degree polynomial expansion with:

$$\alpha = 12{\cdot}6\times10^{-6}\ °C^{-1},$$
$$\beta = 1{\cdot}3\times10^{-9}\ °C^{-2}.$$

(B) Calculate the heating current of this cathode taken to 750°C, knowing it has a circular section of 3·3 mm diameter, a heating voltage of 6·3 V; the conductivity losses will be assumed to be 0·7 W. The total emissivity will be taken equal to 0·35 for the side walls of the cathode cylinder, and to unity for each end.

2. Calculate in l./min the minimum flow of water required for the cooling of transmitting tube anode, knowing:
That it supplies a high-frequency power of 18 kW,
That the efficiency is 75%,
That the filament is heated at 25 V and 80 A and that $^4/_5$ of its power is radiated by the anode,
That the water entering at 20°C must leave at 30°C maximum.

3. A tungsten filament of a length of 100 mm and a diameter of 0·1 mm, mounted in vacuum, is supplied with a current of 1·4 A and a voltage of 12·5 V. What shall be the brightness temperature, read with a disappearing filament pyrometer provided with a filter of $\lambda = 0{\cdot}66\ \mu$?
At this temperature, it will be assumed for tungsten that:

$$\varepsilon_t = 0{\cdot}3, \quad \varepsilon_\lambda = 0{\cdot}43.$$

The conductivity losses at the terminals will be neglected.

4. What is the surface area required for the anode of a receiving tube, which absorbs under static operation 36 mA at 250 V, if the temperature must not exceed 300°C?
It will be assumed:
   (a) That two-thirds of the heating power supplied to the cathode, heated by 6·3 V and 1·1 A, is picked up by the anode.
   (b) That a portion equal to 0·5 W of the anode power is released by conductivity.

   Take $\varepsilon_t = 0{\cdot}8$.

CHAPTER II

1. A cylindrical glass tube of a length $l = 85$ cm, open at both ends, is dipped vertically in mercury so that a length $l' = 32$ cm is immersed. Then the upper end is tightly closed and the tube is lifted so that its lower end is level with the free surface of mercury.

It is then observed that, inside the tube, the mercury level is 17 cm above the external level.

Calculate the value of the atmospheric pressure. Temperature: 22°C.

2. A U-shaped glass tube of a diameter of 1 cm, open at both ends, contains mercury in its curved part, so that the mercury level comes up to 10 cm from the open ends.

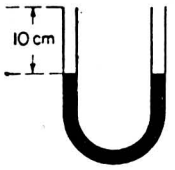


FIG. 1

One end is then sealed and the air contained in it is heated from 20 to 40°C. What will be the change in level of mercury?

3. A metallic bottle of a volume of 50 l. contains nitrogen at a pressure of 150 kg/cm². Calculate the total mass of the gas.
4. State the formula giving the average number of collisions suffered per second by each molecule of a gas, in terms of pressure, temperature, mass and diameter of this molecule. Apply the result obtained:

(a) To a nitrogen molecule at S. T. P. conditions,

(b) To a hydrogen molecule with $p = 10^{-6}$ mm Hg and $t = 200$°C.

5. An electron tube includes a cylindrical cathode with a length of 32 mm and a diameter of 0·85 mm. The bulb has a volume of 85 cm³. The pressure in the tube being 2×10^{-6} mm Hg and the average temperature 250°C, calculate the average number of molecules colliding per second with the cathode. It will be assumed that the residual gas is nitrogen. Are all the given data useful?
6. A thin-walled vessel in which a pump maintains a pressure of 10^{-3} mm Hg is provided with a circular hole of a diameter of 10 μ. How long does it take for 1 g of atmospheric air to pass through the hole?
7. A drum with a diameter of 30 cm and a length of 20 cm rotates at 50 rev/sec inside a fixed cylinder. The clearance between the two cylinders is 0·1 mm. Calculate the couple exerted upon the fixed cylinder (the system is in air at S. T. P. conditions).
8. A flow-meter consists of a wide diameter tube interrupted by a capillary of 10 cm length. An oil manometer indicates the loss of pressure across the capillary.

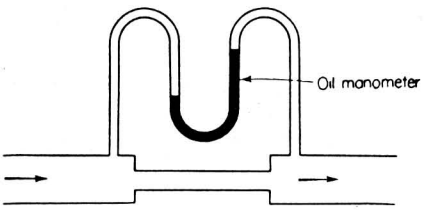


FIG. 2

The gas used being hydrogen at 20°C, what must be the diameter of the capillary in order that a change in oil level of 5 cm corresponds to a flow of 10 l. per min (S. T. P. conditions)?

Remarks: It will be assumed that the flow-meter opens to free air. Oil density: 0·9.

9. An electron tube, supposed to have thin walls, is exhausted down to 10^{-6} mm Hg. The wall is then provided with a little circular hole of a diameter of 1 μ. State the law of the pressure variation in the tube with time.

Apply the result to the case of a bulb volume of 100 cm³ and calculate the time required for the pressure to rise to 750 mm Hg, the external pressure being 760 mm Hg.

CHAPTER III

1. The seven lowest energy levels of sodium vapour are:

   0, 2·11, 3·17, 3·60, 3·75, 4·10 and 4·26 eV.

   This vapour is excited with the help of an ultraviolet radiation of $\lambda = 3{\cdot}300$ Å and the emission of two luminous lines is observed.
   (a) If the wavelength of one of these lines is 5·890 Å, what is the wavelength of the other one?
   (b) Between what energy levels do the electron transitions occur in order to produce these lines?†
2. Caesium vapour is ionized with an ultraviolet radiation of $\lambda = 2{\cdot}537$ Å. What is the maximum speed of the emitted electrons?
3. From the curves of Figs. 2.9 and 3.8, deduce the minimum distance between two flat electrodes raised to a potential difference of 2000 V, in a non-pressurized aeroplane flying at an altitude of 15,000 m, so that no discharge can flash between these electrodes.
4. The beam of a cathode-ray tube has a current of 64 μA at 500 V. The total length of the electron path is 25 cm. The residual gas is nitrogen at a pressure of 10^{-5} mm Hg and a temperature of 25°C.
   The ions produced are assumed to be collected by an electrode raised to a negative voltage with respect to the cathode.
   Knowing the ion current to be $3{\cdot}2 \times 10^{-8}$ A, calculate the ionization probability (average number of ions produced by 100 collisions). Are all the data given of use?
5. Calculate the time taken by a potassium ion, having a velocity corresponding to 100 V, to travel a path of 20 cm. Compare it to the time taken by an electron in the same conditions.

CHAPTER IV

1. A room of $6 \times 4 \times 3$ m contains air saturated with water vapour at 20°C and a pressure of 760 mm Hg.
   (a) What is the total mass of water vapour contained in this room?
   (b) What quantity of water will deposit on the walls when the temperature falls to 0°C?
   Data: Water vapour pressure at 20°C: 17·4 mm Hg; at 10°C: 9·2 mm Hg.
2. The experiment of Fig. 4.2 is carried out. If the barometric tube has a constant diameter of 1 cm, and a total height above the level of mercury in the cup of 1 m, what quantity of ethyl alcohol is to be admitted in order that liquid alcohol begins to appear in the upper chamber?
   Temperature: 20°C; Atmospheric pressure: 760 mm Hg.
3. A tungsten filament has a length of 10 cm and a diameter of 125 μ; it is heated to 2500°C in vacuum. How long does it take to lose by evaporation 10% of its weight?
4. By using the curves of Fig. 4.13, calculate the volume of hydrogen (at S. T. P.) traversing per hour a palladium sheet having a thickness of 0·2 mm and a surface of 3 cm² heated to 275°C.

† Adapted from J. Millman and S. Seely, *Electronics*, McGraw Hill, N. Y., 1941.

5. A piece of aluminium is heated under vacuum and may be assumed to be a sphere of a diameter of 3 mm.
To what temperature must it be heated so that in 30 sec a circular glass plate placed at 30 cm perpendicularly to the direction of the aluminium would be coated with an aluminium film of a thickness of 1 μ?
Calculate the error.

CHAPTER V

1. An evaporation bell-jar of 10 l. in volume is connected to a mercury diffusion pump giving a limiting vacuum of 10^{-3} mm Hg. At zero time, the pressure in the bell-jar is found to be 2×10^{-2} mm Hg. After 15 sec the pressure falls down to $1{\cdot}5 \times 10^{-3}$ mm Hg. Calculate the mean exhaust speed of the pump in this interval.
2. The exhaust speed of an oil diffusion pump is measured by the constant pressure method. The measurement tube has an inner diameter of 0·8 mm. It is observed that at any pressure p included between 10^{-3} and 10^{-5} mm Hg, the shifting velocity u of the index is given in cm/sec, in terms of pressure, by a relation of the form:

$$u = 5170\, p.$$

(a) Calculate the pumping speed in this interval.
(b) Knowing that the pump requires 23 sec to decrease the pressure from 10^{-3} to 10^{-5} mm Hg in a vessel of 60 l., calculate its ultimate pressure.

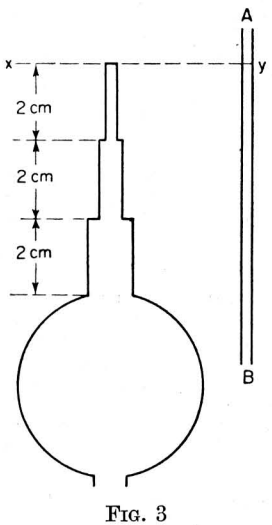


FIG. 3

3. State the formula giving the pumping speed of a two-vane-type pump, in terms of dimensions and of the rotation speed. The secondary effects will be neglected, such as throttling of air at the orifices, etc. However, the thickness of the vanes will be taken into account.
Practical application: Calculate the speed of a two-vane pump with a stator of 12 cm diameter and a rotor of 8 cm diameter; the length of the pump is 15 cm and the rotation speed is 500 rev/min; lastly, the vanes have a thickness of 5 mm.

CHAPTER VI

1. A McLeod gauge with 3 ranges of sensitivity (the Dunoyer pattern) includes a compression bulb with a volume of 200 cm^3. It is surmounted by three compression tubes, with the same length equal to 2 cm, but with decreasing diameters.
In the comparison tube B, mercury rises to XY. What must be the diameter of each compression tube so that, for pressures successively equal to 1 mm Hg, 10^{-2} mm Hg and 10^{-4} mm Hg, mercury comes into the compression tubes to the levels a, b, c, respectively placed in the middle of each tube?
Plot the calibration curve of such a gauge.

2. Consider a triode ionization gauge, the electrodes of which are supposed to be plane and parallel, and to have a common surface of 1·5 cm². The plate raised to + 200 V collects electrons and the grid, polarized at — 10 V, positive ions. The cathode-to-anode distance is 8 mm and the cathode-to-grid distance is 3 mm.
   For an anode current of 20 mA, a grid-current of 1·2 μA is measured.
   Calculate the pressure in the gauge.
   Note: Ionization probability: 25%. Average temperature: 100°C. The gas is assumed to be nitrogen.
   Are all the data of use?

CHAPTER VII

1. A vessel of 6·5 l. is evacuated by a mercury diffusion pump which has an ultimate pressure of 10^{-3} mm Hg.
   The vessel and the pump are connected together by a pipe of 10 cm length and 12 mm diameter.
   How long does it take for the pressure to fall from 10^{-2} to 2×10^{-3} mm? The pump speed is assumed to be constant in this interval and equal to 5 l./sec.
2. An evaporation bell-jar of a volume of 28 l. is evacuated by an oil diffusion pump which has an exhaust speed (supposed constant in the pressure interval mentioned below) of 100 l./sec and an ultimate vacuum of 4×10^{-6} mm Hg. This pump is connected to the bell-jar by a pipe of length 20 cm.
   (a) What must be the minimum diameter of the pipe so that the time necessary to cause the pressure to fall from 10^{-3} to 10^{-5} mm Hg does not exceed 30 sec?
   (b) The same question, the pump speed being 5 l./sec.
   (c) Explain the choice of the formula used to calculate the conductance.
3. Consider a diffusion pump which has to supply an exhaust speed of 20 l./sec at a pressure of 10^{-2} mm Hg. It is backed by a vane-type pump exhausting 3 m³/hr at a pressure of 1 mm Hg.
   Calculate the minimum diameter to give to the pipe connecting both pumps together, its length being 80 cm.

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